# A SYSTEMATIC INTRODUCTION

# ANALYTICAL CHEMISTRY

## AN ELEMENTARY CLASS-BOOK

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# A SYSTEMATIC INTRODUCTION

TO

# ANALYTICAL CHEMISTRY

## AN ELEMENTARY CLASS-BOOK

BY

A. F. WALDEN, M.A.

Lecturer in Chemistry at New College, and Demonstrator in
the University Laboratory, Oxford

AND

B. LAMBERT, M.A.

Merton College, Lecturer and Demonstrator in the
University Laboratory, Oxford

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# PREFACE.

THE following pages are intended to furnish an elementary and systematic introduction to the study of chemical analysis. They represent, substantially, the course of instruction given in our elementary classes to those who are beginners, not in chemistry, but in analysis.

Of late years there has arisen a very natural and proper prejudice against the custom, so long prevalent, of teaching chemical analysis to absolute beginners in the science. But while we are in hearty agreement with the better way which now prevails, of initiating the beginner by a course of 'heuristic' training, including elementary quantitative work, we do not believe that the neglect of qualitative analysis, which has largely followed upon this reform, is either necessary or desirable.

The plan of this book will be obvious at a glance. In a brief introductory chapter we have dealt with some of the underlying ideas of the science of chemical analysis. Then follows a systematic description of the more common metals, with an account of their properties and the reactions of their salts. These are arranged in the familiar analytical 'groups,' and as soon as all the members of any one group have been described we have introduced a discussion of the group as a whole. 'Tables' have not been introduced, the experience of some years demonstrating having convinced us that the blind, unintelligent use frequently made of these is responsible for much, if not all, of the bad results commonly and rightly attributed to 'mere test-tubing.' The student, we hold, must construct his own tables if they are to be of any real value; and we have provided ample material, in the summaries mentioned, for him to do so with the minimum of trouble.

In dealing with the acids, and the reactions of acid radicals, we have mainly followed the lines laid down by Bunsen. In every case the reactions of the salts with dilute hydrochloric acid and with strong sulphuric acid are first considered, and then the reactions in aqueous solution with silver nitrate and with barium chloride (or nitrate) solutions are examined. It is shown how both these methods of investigation afford means of classifying the acid radicals, and detecting that of any particular salt. The acids whose salts are most commonly encountered have been discussed in one chapter (III), while those of less frequent occurrence are placed in a separate chapter (IV), so as to facilitate their omission from an elementary course if desired.

In the fifth chapter we have indicated the way in which a solution should be prepared for analysis, and the general lines upon which that analysis may be successfully conducted.

Reactions in the dry way are considered together in a special chapter (VI), an arrangement which obviates frequent digressions in the general treatment of the earlier chapters, and renders the discussion of this part of the subject less disjointed than it must otherwise be. At the close of this chapter we have discussed the proper relation of tests 'in the dry way' to elementary chemical analysis.

In the final chapter (VII) a brief, but it is hoped a sufficient, discussion of some typical instances of 'totally insoluble' substances is given.

It will be seen that we have assumed the student to be concerned with single substances or simple salts. But the book is so arranged that any teacher who, for the purposes of some particular examination, has to prepare students to analyse easy mixtures can, with very little trouble, adapt it to this purpose.

In the great majority of cases we have, by means of inset notes in smaller type, explained reactions which are likely to present difficulty, and we have also employed similar notes to call attention to points of general interest and importance.

We have, further, tried to prepare the way for a fuller physico-chemical interpretation of reactions, later on, by emphasizing the individuality of the metallic and acidic radicals of salts. To this end, in formulating the various acids and salts, we have enclosed their acidic radicals in brackets.

In conclusion we wish to thank several of our colleagues for suggestions and advice, and, in particular, to acknowledge our indebtedness to Mr. J. C. Thomson, B.A., of Jesus College, for having kindly drawn the diagrams used in Chapter VI.

A. F. W.
B. L.

Chemical Department,
University Museum,
Oxford.

*March, 1908.*

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# A SYSTEMATIC INTRODUCTION TO ANALYTICAL CHEMISTRY.

## CHAPTER I.

### INTRODUCTION.

ACIDS.—From the earliest times chemists have recognized a special class of substances to which the name **acids** has been given. The most striking characteristics of acids, as the term was formerly employed, were

(1) a sharp or sour taste (whence 'acid,' from *acer*, sharp);

(2) power of turning blue vegetable colours red, for instance litmus;

(3) power of acting as solvents for metals, rocks, &c.

It is true that we now apply the term to many substances which display these properties, if at all, in a very slight degree, but it must be remembered that the name 'acid' was originally given to the substances which we now call hydrochloric, nitric, sulphuric, and acetic acids, all of which display them in a very marked manner.

What it is that these substances have in common is

(1) **that all of them contain hydrogen ;**

(2) **that this hydrogen, or some of it, can be removed from them by the action of metallic oxides (or hydroxides);**

(3) **that when so removed, it unites with the oxygen (or hydroxyl) to form water, while its place in the composition of the acid is taken by the metal of the said oxide (or hydroxide).**

Any compound of which these three things are true is now regarded as an **acid.** By far the greater number of such compounds also exhibit the sharp taste, action on vegetable colours, and solvent power originally associated with the term acid. But there are compounds which have no sharp taste, little or no action upon litmus, and no particular power as solvents, which nevertheless come under this wider definition of 'acid.'

ALKALIS.—Chemists also distinguished very early a class of substances having in certain respects OPPOSITE properties to those of acids, particularly a flat soapy taste, and the power of turning red vegetable colours, such as litmus, blue. Such substances were called **alkalis.**

SALTS.—It was soon noticed that, *when an alkali and an acid were brought together in certain quantities, the properties which distinguish both of them disappeared, a substance being produced, which was without action upon either red or blue vegetable colours, and possessed neither the characteristic taste of the acid nor that of the alkali.* Hence the two were said to **neutralize** one another.

The study of the substances formed when acids and alkalis neutralize one another showed them to be very like common salt, and they came to be known as **salts.**

BASES.—It was soon noticed that many substances will neutralize acids which do not themselves possess the distinctive characteristics of alkalis, but that, none the less for this, the products of the neutralization are on the whole similar to common salt, and therefore to be classed as salts.

*To a substance which would neutralize an acid, forming a salt, the name* **base** *was given, and it was soon discovered that these bases are in some way connected with the metals.* Lavoisier showed them to be **oxides of metals.**

We have then the following relationships:—

An ACID is **a compound containing hydrogen** such that

(*a*) **the hydrogen will combine with the oxygen of metallic oxides** (or the hydroxyl of metallic hydroxides) **to produce water ;**

(*b*) **the place of this hydrogen is taken by the metal of the oxide** (or hydroxide) **yielding a salt.**

A BASE is **the oxide** (or hydroxide) **of a metal, capable of reacting as above with acids.**

A SALT is **the product (together with water) of the reaction of acids with bases.**

A salt is thus to be regarded as derived from an acid through *the replacement of the hydrogen of that acid by a metal.* But it is essential that this replacement should be able to be effected through the action of the metallic oxide, with simultaneous production of water. It is true that very many acids (when dissolved in water) are acted upon by many metals with *the setting free of hydrogen* and the production of salts. It is *not* however an *essential* property of *acids* thus to yield free hydrogen when acted upon by metals. There is no more typical 'acid' than nitric acid, yet it is not possible to obtain hydrogen from it by the action of any metal at all, though it does, in solution in water, dissolve most metals with production of their nitrates.

Every **salt**, then, can be referred back to a particular **acid** and **base**, the base in its turn being derived from a particular **metal.**

RADICALS.—Now a study of the properties of **salts** has shown that all those which can be prepared by the neutralization of a particular acid possess certain properties and reactions *in common.* When *nitric acid*, for example, is neutralized by various bases we obtain various different *nitrates*, but *all these nitrates behave exactly alike in certain respects.*

Again, when a particular base, such as copper oxide, for example, is used to neutralize solutions of various different acids, various different salts are formed, but these salts *have certain properties in common.*

Those properties which belong to all the salts derived from any one acid are held to be due to the presence of *that which is left of the acid when the hydrogen is removed.* Thus all the nitrates are derived from the acid $H(NO_3)$ by the replacement of the 'H'-atom:—

$$H(NO_3) + K(OH) = H_2O + K(NO_3)$$
$$2H(NO_3) + CuO = H_2O + Cu(NO_3)_2$$

and the properties common to all nitrates are held to be due to the presence of the group of atoms $(NO_3)$, which is known as **the acid radical** of the nitrates.

Similarly the properties that are common to all the salts formed from any one base are attributed to the presence of *that which is left of that base when the oxygen* (or hydroxyl) *is removed.* This is **the metallic radical.** Thus all the salts derivable from lime (CaO) contain the metallic radical calcium (Ca), and the properties that belong to all of them are regarded as due to this.

DUAL NATURE OF SALTS.—We recognize then, that in every **salt** there are **two parts** which have **separate** and **distinct characteristic properties.** The properties of the salt itself are, in the main, merely the *sum* of

(1) *the properties of its metallic radical,*

and (2) *those of its acidic radical.*

But it is to be noticed that we do not *fully* encounter this **dual character** until the salt is dissolved in water (or other suitable solvent). The characteristic reactions are for the most part reactions in solution. Thus, a solution of copper sulphate exhibits two sets of reactions. In the *first* place, those of 'copper' which are equally well shown by solutions of copper nitrate, copper chloride, copper acetate, or *any other soluble copper salt.* In the *second* place, those of the acid radical of sulphuric acid $(SO_4)$, and these in their turn are equally well shown by solutions of sodium sulphate or aluminium sulphate or *any other soluble sulphate.*

This independent behaviour of the metallic and acidic radicals extends to mixtures of salts in solution. If we mix, for example, lead nitrate and potassium nitrate solutions we shall get a solution exhibiting three sets of reactions—

(*a*) those of 'lead,' common to all lead salts,

(*b*) those of 'potassium,' common to all potassium salts, (*c*) those of the acid radical ($NO_3$), common to all nitrates, and similarly with any other mixture we like to take.

MUTUAL ACTIONS OF SALTS IN SOLUTION.—Consider now a mixture of two solutions such as those of potassium bromide (KBr aq.) and sodium nitrate [$Na(NO_3)$aq.].

> *Note.*—The abbreviation 'aq.' added to the formula of a substance is used, here and throughout this book, to indicate an aqueous solution of the compound in question.

Such a mixture exhibits four distinct sets of reactions, those namely of—

(i) the metallic radical potassium (K),
(ii) the metallic radical sodium (Na),
(iii) the acid radical (Br) of the bromides,
and (iv) the acid radical ($NO_3$) of the nitrates

The same four sets of reactions are equally shown by a mixture of solutions of potassium nitrate [$K(NO_3)$aq.] and sodium bromide (NaBr aq.), for all the possible combinations of the metallic radicals (K) and (Na) and the acidic radicals (Br) and ($NO_3$), viz. KBr, $K(NO_3)$, $Na(NO_3)$, and NaBr, represent salts soluble in water.

As a second case consider the two solutions, potassium bromide, KBr aq., and silver nitrate, $Ag(NO_3)$aq. They possess, **between them,** four distinct sets of reactions, those namely of the metallic radicals (K) and (Ag) and of the acidic radicals (Br) and ($NO_3$). The same reactions, differently distributed, would belong to two solutions of potassium nitrate, $K(NO_3)$aq., and silver bromide, AgBr aq., but here we meet with a difficulty because, though we can get a solution of potassium nitrate, we cannot get one of silver bromide, for silver bromide is insoluble in water. Hence we are not surprised to find that, on mixing, in certain relative quantities, solutions of potassium bromide and silver nitrate, we obtain a **solution** possessing only **two** sets of reactions, those of potassium (K) and of the nitrate radical ($NO_3$), while the insoluble salt, silver bromide, appears in the solid form as a **precipitate.**

$$\text{KBr aq.} + Ag(NO_3)\text{aq.} = K(NO_3)\text{aq.} + \mathbf{AgBr}.$$

Finally, let us take the case of two solutions, one of barium chloride, $BaCl_2$aq., the other of silver sulphate, $Ag_2(SO_4)$aq.

Here again the two possess, **between them**, four distinct sets of reactions, those namely of the metallic radicals (Ba) and (Ag) and of the acidic radicals (Cl) and ($SO_4$). Now the same four sets of reactions, differently distributed, would belong to the two solutions, barium sulphate and silver chloride, but here there is a still greater difficulty, for neither barium sulphate nor silver chloride will dissolve in water. Accordingly we find that when solutions of barium chloride and silver sulphate are mixed, in certain relative quantities, all the four sets of reactions above indicated disappear together from the liquid and two insoluble salts are precipitated—

$$BaCl_2aq. + Ag_2(SO_4)aq. = \mathbf{Ba(SO_4) + 2AgCl.}$$

DOUBLE DECOMPOSITION.—Whenever two salts in solution, by exchange of radicals, produce two new salts they are said to undergo '**double decomposition.**' The type of all double decompositions is—

$$(M)(X) + (N)(Y) = (M)(Y) + (N)(X).$$

In general we cannot tell whether double decomposition occurs or not unless one of the products is either insoluble in water or, though soluble, possesses some distinctive colour. If either of these conditions be fulfilled we can recognize the occurrence of double decomposition either by the formation of a precipitate or by the change in colour which occurs when the solutions are mixed.

Double decomposition is not confined exclusively to pairs of **salts**. It is possible to have double decomposition between a salt and a base or a salt and an acid. In such cases another salt is produced, together with another base or another acid, as the case may be. For example, a solution of nickel chloride and one of potassium hydroxide react to produce a solution of potassium chloride and a precipitate of nickel hydroxide—

$$NiCl_2aq. + 2K(OH)aq. = 2KClaq. + \mathbf{Ni(OH)_2}.$$

A solution of barium chloride and one of sulphuric acid react to form a solution of hydrochloric acid and a precipitate of barium sulphate—

$$BaCl_2aq. + H_2(SO_4)aq. = 2HCl\ aq. + \mathbf{Ba(SO_4)}.$$

ANALYSIS OF SALTS.—Here we have the basis upon which rest most of the reactions employed in analytical chemistry. The science of chemical analysis has for its main object the discovery of the constituent parts, or radicals, of salts.

The surest and easiest way of attaining this end is to apply the above principle of double decomposition so as to produce a characteristic precipitate or, less commonly, a colour change.

Thus, if we wish to know whether a given solution contains the acid radical ($SO_4$) of the sulphates, we add to it another solution known to contain the barium radical (Ba)—for instance, a solution of barium chloride or barium nitrate—and if we obtain a precipitate, and this precipitate has the properties which we know to belong to barium sulphate, $Ba(SO_4)$ (e. g., a white colour, insolubility in acids, &c.), we can safely infer the presence of the radical ($SO_4$). The solution of the barium salt here constitutes a **reagent** for the radical ($SO_4$).

Again, if we desire to discover whether a certain solution contains the acid radical (CNS) of the sulphocyanides, we can either make use of the insolubility (and other known properties) of silver sulphocyanide, Ag(CNS), using a solution of silver nitrate as our reagent, or we can take advantage of the fact that ferric sulphocyanide, $Fe(CNS)_3$, though not insoluble, has in solution an intense red colour. If the addition of ferric chloride solution as reagent determines the appearance of the red colour we can infer that the radical (CNS) is probably contained in the solution under examination.

We have recourse far more often to reactions involving the formation of precipitates than to those involving mere colour changes. We shall, in succeeding chapters, meet with very numerous examples of the former, and with a few of the latter kind.

*Note.*—It was discovered nearly a hundred years ago that, when a current of electricity is passed through a solution of a salt, the salt is decomposed. This decomposition is called **electrolysis.**

Faraday showed that salts, on electrolysis, separate into **two parts** which travel respectively to the two electrodes. He found, further, that at the *anode* (or positive electrode) the *acid radical* makes its appearance, while at the *cathode* (or negative electrode) the *metallic radical* is separated. Sometimes the actual metal or the acidic radical, which travels to the cathode or to the anode as the case may be, simply separates there. Thus copper, silver and many other metals are easily deposited upon cathodes. From solutions of chlorides the element chlorine is actually separated at the anode, two monovalent (Cl) radicals combining to form $Cl_2$, chlorine gas. Sometimes however the metallic or acidic radical liberated at the electrode reacts with the water present. When a solution of sodium sulphate, for example, is electrolysed, the sodium which would be deposited on the cathode reacts with the water to liberate hydrogen and produce sodium hydroxide :—

$$2Na + 2H_2O = 2Na(OH) + H_2,$$

while the $(SO_4)$ at the anode reacts with the water thus :—

$$2(SO_4) + 2H_2O = 2H_2(SO_4) + O_2$$

giving sulphuric acid and oxygen gas.

Because these two parts of the salt thus travel, in opposite directions, through the solution, FARADAY gave them the name **ions** (from the Greek ἰών = going). He called that part which goes to the anode, the **anion**, the other, the **cation**. It is clear from what has been said, that the anion of a salt is its acidic radical, the cation its metallic radical.

Many chemists, especially of late years, have preferred to speak of the '*ions*' of salts where we have spoken of their '*radicals.*' There is no particular advantage to be gained, so far as elementary chemistry is concerned, by borrowing this term from electrochemistry, and we shall continue to use the term 'radical.' It may be useful however to remember that the terms

*metallic radical, metallic ion, cation,* and *positive ion*

are simply different names for the same thing, and that, similarly,

*acidic radical, acid ion, anion,* and *negative ion*

are synonymous terms.

BASICITY OF ACIDS.—We have seen that an acid contains *hydrogen*, hydrogen capable of combining with the oxygen of metallic oxides, and having its place in the composition of the acid taken by the metal.

The molecular weight of any acid must, then, contain at least one atomic weight of hydrogen, or, as it is more usually expressed, the 'molecule' of an acid must contain at least one 'atom' of hydrogen.

*Note.*—The terms 'molecule' and 'atom' are, for the analytical chemist, really abbreviations. By 'molecule' he understands what is better expressed by 'molecular weight' and by 'atom' what is better called 'atomic weight.' *The symbol of each element stands for one atomic weight of that element. The collection of symbols that constitutes the formula of a compound therefore stands for the molecular weight of that compound.* Thus, given the atomic weights

$$K = 39, \ C = 12, \ O = 16,$$

the formula $K_2C_2O_4$ for potassium oxalate indicates that the molecular weight of potassium oxalate is 166.

Of course the molecular weight of an acid may, and frequently does, contain more than one atomic weight of hydrogen. The formulae—

$HCl$, for hydrochloric acid,
$H_2SO_4$, for sulphuric acid,
$H_3PO_4$, for phosphoric acid,

*represent the molecular weights of these acids*, and it is found that, in each case, *the whole of the hydrogen* contained in them can be exchanged for metals with the production of salts.

Acetic acid has a *molecular weight* represented by the formula $C_2H_4O_2$, but it is found that *one only of the four atomic weights of hydrogen is capable of being exchanged for metals* by reaction with metallic oxides. To emphasize this fact we write the formula as $H(C_2H_3O_2)$.

Acids fall naturally into several classes according to the number of atomic weights of replaceable hydrogen contained in their molecular weights.

Thus hydrochloric, nitric, and acetic acids are classed (with many others) as **monobasic acids** because **there is, in the molecular weight of each, one atomic weight of hydrogen,** AND ONLY ONE, **capable of reacting with** BASES **so as to be replaced by metal.**

Similarly sulphuric acid, $H_2(SO_4)$, and oxalic acid, $H_2(C_2O_4)$, and many others, are classed as **dibasic,** while phosphoric acid, $H_3(PO_4)$, affords an example of a **tribasic acid.**

EQUIVALENTS OF ACIDS.—The **equivalent of an acid is that weight of it which contains one unit weight of acidic hydrogen.** It is customary to express these equivalents in grammes. The weight of hydrochloric acid, $HCl$, which contains one gramme of acidic hydrogen is 36·5 grms., and so 36·5 is the equivalent of hydrochloric acid. It should be evident that *the equivalent of any monobasic acid is represented by the molecular weight* (*in grms.*) *of that acid.*

When *dibasic* acids are considered, it must be remembered that *their molecular weights contain, each, two atomic weights of acidic hydrogen,* so that **their equivalent is half the molecular weight.** Sulphuric acid, $H_2SO_4$, has the molecular weight 98, but its equivalent is 49, since 49 grms. of this acid contain one grm. of acidic hydrogen.

Similarly with a *tribasic* acid the equivalent will be *one-third of the molecular weight.* The formula, $H_3PO_4$, for phosphoric acid shows it to have the molecular weight 98, and, since it is tribasic, the equivalent is 32·66, for 32·66 grms. of the acid contain one grm. of acidic hydrogen.

These quantities are called 'equivalents,' because *they represent the weights of these acids which are able to neutralize one and the same weight of a chosen base.* For example, if lime, CaO, be chosen as the base, it is found that

36·5 grms. of hydrochloric acid (HCl),
or 49 grms. of sulphuric acid (half of $H_2SO_4$),
or 32·66 grms. of phosphoric acid (one-third of $H_3PO_4$)

will each neutralize (and be neutralized by) the same weight, 20 grms., of this base.

EQUIVALENTS OF BASES.—We are now enabled to extend the idea of equivalents to *bases.* **The equivalent of any base is the weight of it which will neutralize that weight of any acid in which is contained one unit weight of acidic hydrogen.** In short, **the equivalent of a base is that weight of it which will neutralize one equivalent of any acid.**

For instance, to neutralize

36·5 grms. of hydrochloric acid (HCl),
49 grms. of sulphuric acid (half of $H_2SO_4$),
32·66 grms. of phosphoric acid (one-third of $H_3PO_4$),

requires, in each case,

56 grms. of potassium hydroxide (KOH),
76·5 grms. of barium oxide (half of BaO),
26 grms. of aluminium hydroxide (one-third of $Al(OH)_3$).

These numbers are the equivalents of the three bases named.

EQUIVALENTS OF METALS.—When bases neutralize acids the result is the formation of water and the replacement of the acidic hydrogen by metal. Consider the neutralization of sulphuric acid by aluminium hydroxide. We have seen that the equivalent of sulphuric acid is 49, and that of aluminium hydroxide 26. These are the proportions in which this acid and this base must be taken to neutralize one another. Now 49 grms. of sulphuric acid contain one grm. of hydrogen, and 26 grms. of aluminium hydroxide contain 9 grms. of aluminium. The result of the neutralization is that the 9 grms. of aluminium take the place, in the acid, of the 1 grm. of hydrogen. *We can therefore say that 9 grms. of aluminium are equivalent to 1 grm. of hydrogen*, or, that **the equivalent of aluminium is 9.** In short, **the equivalent of a metal is that weight of it which will replace one unit weight of hydrogen.**

*Note.*—Many metals, such as zinc, magnesium, aluminium, iron, etc., will disolve in dilute acids, such as sulphuric or hydrochloric, with evolution of hydrogen, the place of this hydrogen being taken by the metal. This enables us to determine directly the equivalents of such metals. The hydrogen evolved when a known weight of the metal is dissolved in the acid is collected and measured. The weight of 1 cc. of hydrogen (at 0° C and 760 mms.) is 0·00009 grm., and so the weight of the hydrogen evolved can be calculated from its volume. Hence we can calculate the weight of metal which would displace 1 grm. of hydrogen.

In the case of metals which do not dissolve in dilute acids with evolution of hydrogen, such as mercury or lead, it is enough to determine the weight of the oxide which will neutralize an equivalent of an acid: it contains one equivalent of the metal.

VALENCY.—When the equivalents of the metals come to be compared with their atomic weights, it is noticed that *in some cases the equivalent and the atomic weight are represented by the same number:* this is so for potassium, sodium, and silver.

*In other cases the atomic weight is double the equivalent:* this is the case with zinc, magnesium, and calcium, among others.

*In other cases, again, the atomic weight is three times as great as the equivalent:* this is so for bismuth and aluminium, among others.

In those cases where the atomic weight and the equivalent have *identical* values it is evident that **one atomic weight of the metal replaces one atomic weight of hydrogen** (since an equivalent of any metal is the weight of it which replaces 1 unit weight of hydrogen, and the atomic weight of hydrogen is 1). In other words, *one atom of the metal can, in a chemical change, take the place of one atom of hydrogen.* **Such metals are said to be monovalent.**

When the value of the equivalent is *half* that of the atomic weight, then *one atomic weight of the metal must take the place of two atomic weights of hydrogen.* In other words, *one atom of the metal must be able to replace two atoms of hydrogen.* Such metals are said to be **divalent.**

When the value of the equivalent is *one-third* that of the atomic weight, it follows, similarly, that *one atom of the metal must be able to replace three atoms of hydrogen*, and the metal is **trivalent.**

A metal whose equivalent is one-fourth of its atomic weight is **tetravalent,** and so on.

> *Note.*—Several of the metals possess *more than one equivalent* For example, in the ferrous salts 28 grms. of iron take the place of 1 grm. of hydrogen in acids; while in the ferric salts 18·66 grms. of iron replace 1 grm. of hydrogen in acids. Now the atomic weight of iron is 56, and so, in the ferrous salts iron is *divalent,* and in the ferric salts it is *trivalent.* A metal may thus have more than one valency.

When we have to do with substances other than metals, which do not displace hydrogen but combine with it, for instance non-metals like chlorine, oxygen, and nitrogen, we define their valency by *the number of atoms of hydrogen with which their atom can combine.* Thus chlorine is monovalent because its hydride has the formula $HCl$, oxygen divalent because its hydride has the formula $H_2O$, and nitrogen trivalent because its compound with hydrogen has the formula $H_3N$.

The valencies of the acid radicals follow from the formulae of the acids themselves. The $(SO_4)$ of sulphates is manifestly divalent, because it combines with two atoms of hydrogen to form $H_2(SO_4)$. In short, **the valency of an acid radical is expressed by the same number as the basicity of its acid.**

ACID SALTS.—When the basicity of an acid is greater than unity it is possible that a part only of its acidic hydrogen may be removed and replaced by metals. Thus sulphuric acid, when it reacts with potassium hydroxide, may either be completely neutralized—

$$H_2(SO_4) + 2K(OH) = K_2(SO_4) + 2H_2O$$

to give the neutral salt, potassium sulphate, or it may react with half this quantity of the base—

$$H_2(SO_4) + K(OH) = KH(SO_4) + H_2O$$

to give an *acid salt*, potassium hydrogen sulphate or acid potassium sulphate.

BASIC SALTS.—We have seen that some bases (potassium hydroxide, for example) have equivalents equal to their molecular weights. Others (zinc hydroxide, for instance) have equivalents which are one half of their molecular weights, while others (like aluminium hydroxide) have equivalents one-third of their molecular weights.

To neutralize completely the molecular weight of a base like zinc hydroxide requires two equivalents of an acid—

$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O.$$

If this same base reacts with only one equivalent of the acid the neutralization is incomplete, and a *basic salt* is formed—

$$Zn(OH)_2 + HCl = Zn(OH)Cl + H_2O.$$

Several instances of basic salts will be found in later chapters.

---

USE OF SYMBOLS.—In the following pages wherever the symbol of a metallic or acidic radical is used alone the *valency* of that radical is indicated by *dots* in the case of *metallic*, and by *dashes* in the case of *acidic* radicals. Thus the metallic radical calcium is distinguished as $Ca^{\cdot\cdot}$, and the acid radical of phosphoric acid and the phosphates as $(PO_4)'''$. This use of dots and dashes with the symbols has become conventional, The habit of using symbols to represent the actual elements themselves is much to be deprecated. The element chlorine may perhaps be denoted by the formula $Cl_2$, inasmuch as this formula indicates the molecular quantity (71 parts by weight) of that element, but Cl is merely a symbol which must not be used alone. In the form $Cl'$ it may be used as an abbreviation for 'the acid radical of hydrochloric acid and the chlorides.'

Having now gained some idea of the meanings of the terms in common use and of the main principles involved in the practice of analysis, we shall proceed to study the more important reactions of the commoner metals and acid radicals and to see how they may be classified.

# CHAPTER II.

## STUDY OF THE COMMONER METALS.

### I.

SILVER.—Symbol **Ag** (*Argentum*); Atomic Weight **108.**
**Monovalent.**

**Formulae of chief compounds** :—

Oxide $Ag_2O$ [Hydroxide $Ag(OH)$]
Chloride $AgCl$ Nitrate $Ag(NO_3)$
Sulphate $Ag_2(SO_4)$.

**Properties of the metal.**—Silver is a white metal, fairly hard, ductile, very malleable, with a high melting point (950°C).

**Action of air (or oxygen).**—Silver does not undergo oxidation either at ordinary temperatures or when heated. The molten metal absorbs oxygen gas, but gives it out again as it cools.

**Action on water.**—*None.*

**Action of acids** :—

*Unacted upon* by hydrochloric acid or dilute sulphuric acid.

**Dissolved** by **nitric acid** (suitably diluted with water) with formation of silver nitrate solution and evolution of nitric oxide—

$$3Ag + 4H(NO_3) = 3Ag(NO_3) + 2H_2O + NO.$$

*Acted upon* by *hot concentrated sulphuric acid* with formation of silver sulphate and water and evolution of sulphur dioxide—

$$2Ag + 2H_2(SO_4) = Ag_2(SO_4) + 2H_2O + SO_2.$$

## Reactions of Silver Salts in Solution.

[Use a solution of silver nitrate.]

(1) **Dilute Hydrochloric Acid** produces a *white* curdy precipitate of silver chloride (AgCl) which is *insoluble in excess of the reagent.* This precipitate turns gradually violet on exposure to light. When well shaken it collects into a lump. Examine it further, as follows:—

(*a*) Pour off the supernatant liquid, add 7 or 8 ccs. of water and *boil.* The precipitate does not dissolve: silver chloride is insoluble in water, even boiling water.

(*b*) Pour away the water, add 5 or 6 ccs. of *ammonia* solution and again shake. The precipitate dissolves: *silver chloride is soluble in ammonia.*

yellowish white

(2) **Potassium Iodide solution** gives a *pale yellow* precipitate of silver iodide (AgI), which resembles the chloride except in colour, but is *insoluble* in *ammonia.* [Try it, and contrast with the chloride.]

(3) **Potassium Chromate solution** gives a *dark red* precipitate of silver chromate, $Ag_2(CrO_4)$. Let this settle, pour off the liquid, add 5 or 6 ccs. of dilute nitric acid, shake and warm. The precipitate dissolves: *silver chromate is soluble in dilute nitric acid.*

(4) **Potassium Cyanide solution** [add *very slowly*] gives a *white* precipitate of silver cyanide, Ag(CN), *which readily dissolves again in an excess of the reagent.*

*Reactions:*

$$Ag(NO_3) + K(CN) = K(NO_3) + \mathit{Ag(CN)} \text{ [insoluble]}.$$
$$\mathit{Ag(CN)} + K(CN) = KAg(CN)_2 \text{ [soluble]}.$$

This solution is important because it is employed in electroplating with silver.

(5) **Action of ammonia on compounds of silver.**—With the exception of the iodide, the compounds of silver readily combine with ammonia to form substances soluble in water. Hence even those which are themselves insoluble in water will dissolve in ammonia solution, as was illustrated in the case of the chloride above. The oxide is another case

in point, and '*ammoniacal silver oxide solution*' is sometimes useful as a reagent. To prepare it, take some of the bench ammonia solution and dilute it with about 20 times its volume of water. Add this diluted solution very gradually to one of silver nitrate. A *brown* precipitate, which consists of *silver oxide*, $Ag_2O$, is first produced, and on adding, cautiously, a drop or two more of the ammonia, this *dissolves* again. The resulting 'ammoniacal silver oxide solution' is very useful as a test for certain reducing agents, i.e. substances that can take oxygen from bodies containing it. In this case the oxygen is taken from the dissolved silver oxide, leaving metallic silver which—being insoluble in ammonia—is deposited. Among the reducing agents which readily effect this change are the salts of tartaric acid.

(6) **Production of a silver mirror.**—Take the ammoniacal silver oxide solution just prepared and add to it a few drops of a solution of **sodium or potassium tartrate.** Shake the mixture and **warm gently.** Observe the deposition of metallic silver upon the glass.

## II.

### LEAD.—Symbol **Pb** (*Plumbum*); Atomic Weight **207.**

### Divalent.

**Formulae of chief compounds:—**

| | |
|---|---|
| Oxide $PbO$ (litharge) | Hydroxide $Pb(OH)_2$ |
| Chloride $PbCl_2$ | Nitrate $Pb(NO_3)_2$ |
| Sulphate $Pb(SO_4)$ | Carbonate $Pb(CO_3)$ |

In addition to the ordinary basic oxide, PbO, which by its reaction with acids gives rise to the salts of this metal, there are two other important oxides of lead. These have the formulae $Pb_3O_4$ and $PbO_2$ and the names *red lead* and *lead peroxide* respectively. The former is produced when litharge (PbO) is heated to the required extent in the air. The dioxide, $PbO_2$, is left as a residue when red lead is acted upon by dilute nitric acid (see below). This dioxide, when it reacts with many acids, yields the salt derived from the lower oxide

PbO and either oxygen or the product of the action of oxygen upon the acid, e.g.

$$\left\{\begin{array}{l} PbO_2 + 2HCl = PbCl_2 + H_2O + [O] \\ 2HCl + [O] = H_2O + Cl_2 \end{array}\right\}$$

$$\text{or } PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2.$$

This behaviour justifies its description as a peroxide.

**Properties of the metal.**—Lead is a bluish-white metal, bright when freshly cut, but rapidly tarnishing in the air. It is very soft, easily marking paper, and is malleable. It melts at a comparatively low temperature (334°C).

**Action of air (or oxygen).**—When cold, the surface only is slightly oxidized in air, becoming dull grey. But melted lead gradually absorbs oxygen to form the oxide, PbO (litharge). If the litharge be further heated in a good supply of air it can absorb some more oxygen to form '*red lead*,' $Pb_3O_4$. When this is still more strongly heated it evolves oxygen and is reconverted into litharge.

**Action on water.**—Lead has very little action on *pure* water. A small quantity of the metal passes into solution as lead hydroxide, $Pb(OH)_2$, but with ordinary 'hard' water this does not happen. Traces of lead can often be recognized in soft water that has passed through lead pipes.

**Action of Acids.**—Lead is *unacted upon* by hydrochloric or dilute sulphuric acids.

It is **attacked** by **nitric acid** (suitably diluted with water) with production of lead nitrate and evolution of nitric oxide—

$$3Pb + 8H(NO_3) = 3Pb(NO_3)_2 + 4H_2O + 2NO.$$

If the nitric acid be fairly strong the lead nitrate is deposited as a crystalline powder, for this salt, though soluble in water, is almost insoluble in nitric acid. In presence of enough water it dissolves and a solution of lead nitrate is thus obtained.

The metal is *slowly dissolved* by hot concentrated sulphuric acid, the solution giving a white precipitate of lead sulphate, when poured, after cooling, into water.

## Reactions of Lead Salts in Solution.

[Use a solution of lead nitrate or lead acetate.]

(1) **Dilute Hydrochloric Acid** produces a *white* crystalline precipitate of *lead chloride*, $PbCl_2$, which is *insoluble in excess of the reagent.* This precipitate does not change on exposure to light nor form a clot when it is shaken (contrast with silver chloride).

Examine it further by allowing it to settle, pouring off the supernatant liquid, adding a few ccs. of water, and boiling. The precipitate dissolves: *lead chloride is soluble in boiling water.* On allowing this solution to cool the $PbCl_2$ may be seen gradually to separate again in crystals.

(2) **Potassium Iodide solution** gives a *canary-yellow* precipitate of *lead iodide*, $PbI_2$. If the supernatant liquid, and most of the precipitate, be poured away it will be found that the remainder of the precipitate can be *dissolved in boiling water*, yielding a colourless solution. On allowing this solution to cool the lead iodide gradually crystallizes out in iridescent spangles (contrast $PbI_2$ with AgI).

(3) **Potassium Chromate solution** yields a *yellow* precipitate of *lead chromate*, $Pb(CrO_4)$. Let this settle, pour off the supernatant liquid, add **lime-water,** in large excess, and boil. The *yellow* precipitate gradually *becomes red.* This is due to the formation of 'basic lead chromate.'

*Note.*—The yellow $Pb(CrO_4)$ is the pigment 'chrome yellow.' The red salt $Pb(CrO_4) . Pb(OH)_2$ is 'chrome red'—

$$2Pb(CrO_4) + Ca(OH)_2 = Pb_2(CrO_4)(OH)_2 + Ca(CrO_4).$$

(4) **Hydrogen Sulphide solution** produces a *black* precipitate of *lead sulphide*, PbS, which is insoluble in cold dilute acids.

(5) **Dilute Sulphuric Acid** gives, even in very dilute solutions of lead salts, a *white* precipitate of *lead sulphate*, $Pb(SO_4)$.

The production of beads of metallic lead when the compounds of this element, mixed with sodium carbonate, are heated on charcoal in the reducing flame, is described under 'Reactions effected with the blow-pipe flame' in Chapter VI below.

## *ADDENDUM.*

**Action of acids on 'red lead.'**—Heat a few ccs. of dilute nitric acid to boiling in a test-tube and drop into it a small pinch of red-lead. Notice that the scarlet colour disappears and that a dark brown powder settles to the bottom. Pour off the clear liquid into another test-tube, and, to separate portions of it, apply tests (4) and (5) above. These will show that a portion of the red lead has been dissolved. The dark coloured residue is lead peroxide $PbO_2$—

$$Pb_3O_4 + 4H(NO_3) = 2Pb(NO_3)_2 + 2H_2O + PbO_2.$$

## III.

### MERCURY.—Symbol **Hg** (*Hydrargyrus*); Atomic Weight **200**. **Divalent.**

This metal forms two oxides and two corresponding series of salts, that is to say there are *two basic oxides of mercury.* These oxides are :—

**mercurous** oxide $Hg_2O$—black ;
**mercuric** oxide $HgO$—red.

The salts are derived from them by their reaction with acids, water being eliminated, in the usual way.

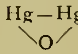
**Formulae of chief compounds :—**

**Mercurous**

| | |
|---|---|
| Oxide $Hg_2O$ | [Hydroxide $Hg_2(OH)_2$] |
| Chloride $Hg_2Cl_2$ (*Calomel*). | Nitrate $Hg_2(NO_3)_2$ |
| | Sulphate $Hg_2(SO_4)$. |

**Mercuric**

| | |
|---|---|
| Oxide $HgO$ | [Hydroxide $Hg(OH)_2$] |
| Sulphate $Hg(SO_4)$ | Nitrate $Hg(NO_3)_2$ |
| Sulphide $HgS$ | Chloride $HgCl_2$ (*Corrosive Sublimate*) |

*Note.*—The ending *-ous* applied to mercurous salts is the anglicised form of the Latin *-osus*, meaning 'full of.' Its use indicates that the *mercurous* salts contain (as their formulae show) *a larger proportion of mercury* than the other class. It might be supposed that in mercurous oxide the mercury was monovalent, thus :—Hg — O — Hg, but it has been proved that mercurous chloride has, when dry, a vapour-density nearly 235 times that of hydrogen so that its molecular weight must be about 470 and its formula $Hg_2Cl_2$. This is therefore represented as Cl—Hg—Hg—Cl and the oxide as  the metal being regarded as always *divalent.*

**Properties of the metal.**—Mercury is a silver-white *liquid* metal, familiar as the 'quicksilver' employed in thermometers and barometers. It is very dense (13·6 grms. per cc.) and remarkably mobile. It boils at a moderate temperature (360°C) and the vapour readily condenses again, forming a mirror-like layer upon a cold surface.

**Action of air (or oxygen).**—At ordinary temperatures mercury does not undergo oxidation, but near its boiling point it is *slowly* oxidized to the red mercuric oxide, HgO (Lavoisier's experiment). At higher temperatures this oxide darkens in colour and then decomposes again into the metal and oxygen (Priestley, 1774).

**Action on water.**—*None.*

**Action of Acids.**—Mercury is *unacted upon* by hydrochloric or dilute sulphuric acid.

It is **dissolved** by **nitric acid** (suitably diluted with water) with evolution of nitric oxide and production of *either* mercurous *or* mercuric nitrate according to the conditions. If the metal be present in excess, and the mixture be not heated, **mercurous** nitrate is gradually formed, and crystallizes out. But if there be more than enough acid entirely to dissolve the metal, and the solution be heated, only **mercuric** nitrate is produced.

The metal is *attacked* by hot concentrated sulphuric acid with formation of mercuric sulphate and evolution of sulphur dioxide

$$Hg + 2H_2(SO_4) = Hg(SO_4) + 2H_2O + SO_2$$

*Notes.*—(i) The *solvent* for metallic mercury is nitric acid and, from what has been said, it will be seen that this first produces **mercurous** nitrate :—

$$6Hg + 8H(NO_3) = 3Hg_2(NO_3)_2 + 4H_2O + 2NO.$$

If, however, this mercurous nitrate be heated with more *nitric acid* the latter acts as an *oxidizing agent*, supplying oxygen :—

$$2H(NO_3) = H_2O + 2NO + [O],$$

which then, with the mercurous nitrate and more nitric acid still, gives rise to the mercuric salt

$$Hg_2(NO_3)_2 + 2H(NO_3) + [O] = 2Hg(NO_3)_2 + H_2O.$$

Thus the transformation of mercurous into mercuric nitrate is *a process of oxidation,* the nitric acid being simultaneously *reduced* to nitric oxide.

(ii) Metallic mercury can also be dissolved in *aqua regia* (a mixture of 4 volumes of concentrated hydrochloric acid with 1 volume of concentrated nitric acid). This mixture produces chlorine :—

$$2H(NO_3) = H_2O + 2NO + [O],$$

$$2HCl + [O] = H_2O + [2Cl],$$

and the chlorine attacks the mercury forming (soluble) mercuric chloride

$$Hg + [2Cl] = HgCl_2.$$

## Reactions of Mercurous Salts in Solution.

[Use a solution of mercurous nitrate.]

(a)

(1) **Dilute Hydrochloric Acid** produces a heavy *white* precipitate of *mercurous chloride* (**calomel**), $Hg_2Cl_2$, *insoluble in excess of the reagent.* Examine this precipitate further as follows :—

(*a*) Allow it to settle, pour off the supernatant liquid, add *water* and *boil.* The precipitate does not dissolve : *calomel is insoluble in water.*

[Note resemblance to AgCl and difference from $PbCl_2$].

(*b*) Allow to settle again, pour off the water, add 5 or 6 ccs. of *ammonia* solution and shake. The precipitate turns black : **calomel is blackened by ammonia.** [Difference from AgCl].

*Note.*—This blackening under the influence of ammonia *is characteristic of all* **mercurous** *salts.* The black compounds formed are of somewhat complex character.

(b)

(2) **Potassium Iodide solution** gives a *green* precipitate of *mercurous iodide*, $Hg_2I_2$. If more of the reagent be added this green mercurous iodide is changed to *grey* metallic *mercury.*

*Note.*—The mercurous iodide is decomposed into mercury and mercuric iodide, $Hg_2I_2 = Hg + HgI_2$, and the latter dissolves in the excess of KI aq.

[Contrast with AgI and $PbI_2$].

(3) **Potassium Chromate solution** gives a *brick-red* precipitate of *mercurous chromate*, $Hg_2(CrO_4)$ which is insoluble in dilute nitric acid, even on heating.

[Contrast $Ag_2(CrO_4)$].

These are the most characteristic reactions of *mercurous* salts. Other reactions of mercury salts will be found, under mercuric compounds, below.

## IV.

## GROUP I.

The three classes of salts so far described, the mercurous salts and those of silver and lead, have one property in common, a property moreover which does not belong to any of those that will follow. It is that *their solutions yield, with dilute hydrochloric acid, a white precipitate which is insoluble in excess of the reagent.*

This fact enables us to arrange the metallic radicals in two classes, those which do exhibit this reaction and those which do not.

The radicals $Ag^{\cdot}$, $Pb^{\cdot\cdot}$ and $Hg_2^{\cdot\cdot}$, in fact, constitute a 'group' which is known to analysts as **Group I,** and if their characteristic reaction with dilute hydrochloric acid be observed with a solution of a salt it is safe to infer the presence of one of them. Further, an examination of the white precipitate obtained with (excess of) dilute hydrochloric acid will enable us to decide with practical certainty which of the three is present.

The following scheme, all the details of which are given in the foregoing pages, will indicate how this may be done :—

If dilute hydrochloric acid has produced a white precipitate which is insoluble in excess of the reagent such precipitate must be either

*lead chloride* or *silver chloride* or *mercurous chloride.*

Allow the precipitate to settle, pour off the liquid above it, add several ccs. of *water* and *boil.*

(*a*) Should the precipitate dissolve it is lead chloride.

Apply to portions of the original solution any of the other tests, (2) to (5) given under lead salts.

(*b*) If the precipitate remains undissolved it may be either silver chloride or mercurous chloride.

In the latter case allow it to settle again, pour away the water, add 5 or 6 ccs. of *ammonia* solution and shake.

(*c*) Should the precipitate *dissolve* it is silver chloride.

Apply to portions of the original solution tests (2) and (3) given under silver salts.

(*d*) Should the precipitate *not dissolve* but *turn black* it is mercurous chloride.

Apply to portions of the original solution tests (2) and (3) given under mercurous salts.

If dilute hydrochloric acid does *not* produce a precipitate at all, or if it produces one which dissolves again on adding an excess of the reagent, neither of the radicals $Pb^{\cdot\cdot}$, $Ag^{\cdot}$ or $Hg_2^{\cdot\cdot}$ can be present and the metallic radical of the salt must be sought among those which follow.

*Note.*—Dilute hydrochloric acid may produce a yellow precipitate (becoming dense on *warming*), with simultaneous evolution of sulphur dioxide. In this case the salt is a *thiosulphate* (see Thiosulphates in Chapter IV below). The mixture should be boiled till free of $SO_2$, and the sulphur filtered off. The solution is then fit for analysis.

## V.

### MERCURY.—*Continued.*

### Reactions of Mercuric Salts in Solution.

[Use a solution of mercuric nitrate or chloride].

(1) The solution **acidified with dilute hydrochloric acid** yields with **hydrogen sulphide** solution [*add this very gradually and shake after each addition*] a precipitate which is at first *white*, then turns *yellow-brown* and finally, with excess of the reagent, becomes *black mercuric sulphide* HgS.

Allow this precipitate to settle, pour off the liquid, add excess of *yellow ammonium sulphide* solution and warm gently. The precipitate remains *undissolved* and unchanged.

> *Note.*—The *white* precipitate first obtained is a sulphochloride of mercury
>
> $$Hg_2SCl_2 \text{ (i.e. } Cl-Hg-S-Hg-Cl\text{)}.$$
>
> The excess of $H_2S$ gradually transforms it all into black $HgS$. These colour-changes are absolutely characteristic.

(2) **Potassium iodide solution** gives a precipitate which is at first *salmon pink* and rapidly becomes *scarlet.* This is *mercuric iodide,* $HgI_2$. [Care must be taken with this test because mercuric iodide is soluble in excess of either the mercuric salt or the potassium iodide solution.]

(3) **Stannous chloride solution** gives a *white* precipitate of *mercurous chloride* (calomel) which, on adding more of the reagent and warming gently, changes to *dark grey* metallic *mercury.*

> *Note.*—This production of *mercurous* chloride and, ultimately, of mercury itself, from a mercuric salt is an instance of *reduction.* The mercuric salt corresponds to the oxide $HgO$ and the calomel which is first precipitated to the oxide $Hg_2O$. The reaction may be represented as occurring in the following stages:—
>
> (*a*) production of mercuric chloride by double decomposition
>
> $$Hg(NO_3)_2 + SnCl_2 = HgCl_2 + Sn(NO_3)_2,$$
>
> (*b*) *reduction* of mercuric chloride to mercurous chloride
>
> $$2HgCl_2 + SnCl_2 = \mathit{Hg_2Cl_2} + SnCl_4,$$
>
> (*c*) further *reduction* of mercurous chloride to mercury
>
> $$Hg_2Cl_2 + SnCl_2 = 2\mathit{Hg} + SnCl_4.$$
>
> That stages (*b*) and (*c*) really do represent *reductions* follows from the fact that *the relative proportion of metal in the product is increased* each time. The stannous chloride is, at the same time, converted into stannic chloride and thus its *relative proportion of metal is lowered,* a fact which is expressed by saying that the stannous is *oxidized* to stannic chloride, for the $SnCl_2$ corresponds to an oxide $SnO$ and the $SnCl_4$ to an oxide $SnO_2$.
>
> This use of the terms reduction and oxidation should be noticed carefully.

There is one **mercuric** salt, the **cyanide,** $Hg(CN)_2$, which is anomalous in its behaviour. It gives reaction (1) but not the other reactions of the mercuric salts. However its behaviour when heated alone in an ignition tube is so characteristic that there should be no difficulty in recognizing it. The salt, which is a white crystalline solid, soluble in water, breaks up into metallic mercury, which is deposited as a mirror on the cooler parts of the tube, and cyanogen gas, $C_2N_2$, which is combustible and, if lighted, burns at the mouth of the tube with a splendid purple-red flame.

### *ADDENDUM.*

**Reaction common to all mercury salts** (whether mercurous or mercuric).

On to a strip of **clean bright copper foil** pour a few ccs. of the solution to be tested for mercury, and acidify with a few drops of dilute nitric acid. Let the whole stand for several minutes. Take out the strip (having poured away the liquid) dry it with a piece of filter paper and rub it very gently. It will, if mercury be present, be coloured *bright silver-white.*

> The copper has been covered with a coating of metallic mercury, and is said to be 'amalgamated.' The chemical reaction is simply that some of the copper goes into the solution, replacing an equivalent amount of mercury in the salt, and the mercury thus set free coats the rest of the copper.

The behaviour of mercury compounds when heated in an ignition tube is noteworthy (see Chapter VI below).

## VI.

## COPPER.—Symbol **Cu** (*Cuprum*); Atomic Weight **63·5.**

## **Divalent.**

This metal forms two oxides, and two corresponding series of salts, that is to say there are *two basic oxides of copper.* These oxides are, respectively, the red **cuprous** oxide, $Cu_2O$, and the black **cupric** oxide, $CuO$. The salts are derived from these by their reaction with acids, water being eliminated, in the usual way.

**Formulae of chief compounds** :—

1. **Cuprous** Oxide $Cu_2O$ [Hydroxide $Cu_2(OH)_2$]
Chloride $Cu_2Cl_2$ Cyanide $Cu_2(CN)_2$
Iodide $Cu_2I_2$

**2. Cupric**
Oxide $CuO$
Chloride $CuCl_2$
Sulphate $Cu(SO_4)$
Sulphide $CuS$
Hydroxide $Cu(OH)_2$
Nitrate $Cu(NO_3)_2$
Carbonate $Cu(CO_3)$

Of the *cuprous* compounds only the oxide, iodide and cyanide are stable in the air. The chloride, which (like silver chloride) is white and insoluble, absorbs oxygen greedily, yielding a green oxy-chloride. No cuprous salt is stable *in solution*, so we shall not be called upon to study their reactions. The copper is regarded as divalent in the cuprous salts just as mercury is in the mercurous compounds.

*Note.*—It is noteworthy, in view of this instability—really oxidizability—of most cuprous salts, that the cyanide $Cu_2(CN)_2$ and iodide $Cu_2I_2$ should not only be fairly stable but should be the only known compounds of copper with cyanogen and with iodine. If it be attempted to make cupric cyanide or cupric iodide by double decomposition between cupric sulphate and potassium cyanide or iodide solutions the reactions

$$2Cu(SO_4) + 4K(CN) = Cu_2(CN)_2 + C_2N_2 + 2K_2(SO_4)$$

and $$2Cu(SO_4) + 4KI = Cu_2I_2 + I_2 + 2K_2(SO_4).$$

take place, and the cuprous salt, together with free cyanogen gas or free iodine as the case may be, is formed.

**Properties of the metal.**—Copper is a red metal, fairly hard, exceedingly tough and malleable. It has a very high melting-point (above 1000° C).

**Action of air (or oxygen).**—At ordinary temperatures copper is not affected by exposure to air. When heated moderately it is oxidized superficially, becoming covered with a thin layer of cuprous oxide which produces a fine play of colours. When more strongly heated it is converted into black cupric oxide.

**Action on water.**—*None.*

**Action of acids.**—Copper is *not acted upon* by dilute sulphuric acid, and is practically *unattacked* by hydrochloric acid.

It is **dissolved** by **nitric acid** (suitably diluted with water) with formation of cupric nitrate solution and evolution of nitric oxide :—

$$3Cu + 8H(NO_3) = 3Cu(NO_3)_2 + 4H_2O + 2NO$$

It is *acted upon* by *hot concentrated sulphuric acid* with production of cupric sulphate and evolution of sulphur dioxide

$$Cu + 2H_2(SO_4) = Cu(SO_4) + 2H_2O + SO_2.$$

*Notes.*—(i) Compare these reactions with those of the corresponding acids on silver and mercury.

(ii) In the case of copper the equation given for the action of strong sulphuric acid does not represent all that occurs. A black mass, containing cuprous sulphide, is also produced.

(iii) By boiling copper for a long time with strong hydrochloric acid it is possible to dissolve *a very little*. Hydrogen is evolved and a solution of cuprous chloride in hydrochloric acid is formed.

(iv) Aqua regia (see Note (ii) on p. 21) will dissolve the metal yielding a dark-coloured solution of *cupric* chloride. If this be evaporated so as to expel the excess of acid and then diluted with water a solution of cupric chloride, which is green or blue according to concentration, is obtained.

## Reactions of Cupric Salts in Solution.

[Use a solution of copper sulphate or nitrate.]

(1) The solution, **acidified with dilute hydrochloric acid** yields, with **hydrogen sulphide** solution, a *dark brown* (or *black*) precipitate of *cupric sulphide*, CuS.

Allow this precipitate to settle, pour off the liquid, add excess of *yellow ammonium sulphide* solution and warm gently. The precipitate remains *undissolved* and unchanged.

(2) **Ammonia solution** (add *very* little at first) produces a *pale blue* precipitate containing *cupric hydroxide*, $Cu(OH)_2$, which is very easily soluble in excess of the reagent yielding *a deep blue solution.*

(3) **Potassium Ferrocyanide solution** added to a very much diluted solution of a copper salt which has been acidified with dilute hydrochloric acid gives a *chocolate-brown* precipitate of *cupric ferrocyanide* $Cu_2[Fe(CN)_6]$.

(4) A piece of **bright iron** (e.g. a piece of iron wire, cleaned with emery paper) placed in a solution of a copper salt becomes covered with a *red deposit of metallic copper*—

$$Cu(SO_4) + Fe = Fe(SO_4) + Cu.$$

*Note.*—The reactions of copper compounds 'in the dry way,' viz. (1) colouration of borax bead,

(2) colouration of Bunsen flame, and

(3) reduction, on charcoal, to the metallic state also afford valuable tests. They are described in Chapter VI below.

## VII.

## BISMUTH.—Symbol **Bi**; Atomic Weight **208**.

## Trivalent.

**Formulae of chief compounds:—**

| | |
|---|---|
| Oxide $Bi_2O_3$ | Hydroxide $Bi(OH)_3$ |
| Chloride $BiCl_3$ | Nitrate $Bi(NO_3)_3$ |
| Sulphate $Bi_2(SO_4)_3$ | Sulphide $Bi_2S_3$. |

As these formulae show, the normal bismuth salts are derived from the oxide $Bi_2O_3$ by the elimination of its oxygen, as water, with the hydrogen of acids. But in addition to these normal salts there are also *basic salts* of bismuth in which this elimination of oxygen is incomplete. These basic salts contain the monovalent atomic grouping $(BiO)^{\cdot}$ to which the name 'bismuthyl' is given. Thus, in addition to the soluble chloride, $BiCl_3$, and nitrate, $Bi(NO_3)_3$, there exist also a basic chloride $(BiO)Cl$ and a basic nitrate $(BiO)(NO_3)$ which are insoluble in water [see reaction (3) below].

**Properties of the metal.**—Bismuth is a white metal with a reddish tinge. It is highly crystalline, very brittle and easily powdered. It melts at a lower temperature (268°C) than lead, and is harder than that metal; it does not mark paper.

**Action of air (or oxygen).**—At ordinary temperatures bismuth is not affected by exposure to air. When heated it oxidizes superficially, even at 200°, and when melted, slowly turns into the oxide, $Bi_2O_3$.

**Action on water.**—Bismuth does not act upon liquid water, hot or cold, but at a red heat the molten metal slowly decomposes steam liberating hydrogen and forming the oxide,

$$2Bi + 3H_2O = Bi_2O_3 + 3H_2.$$

**Action of acids.**—Neither hydrochloric acid nor dilute sulphuric acid will attack the metal.

It is **dissolved** by **nitric acid** (suitably diluted with water) with formation of bismuth nitrate solution and evolution of nitric oxide.

It is *acted upon* by *hot concentrated sulphuric acid* with formation of the sulphate and evolution of sulphur dioxide.

### Reactions of Bismuth Salts in Solution.

[Use a solution of bismuth nitrate.]

(1) The solution, **acidified with dilute hydrochloric acid**, yields, with **hydrogen sulphide** solution, a *dark brown* (or *black*) precipitate of *bismuth sulphide*, $Bi_2S_3$.

Allow this precipitate to settle, pour off the liquid, add excess of *yellow ammonium sulphide* solution and warm gently. The precipitate remains *undissolved* and unchanged.

(2) **Ammonia solution** gives a *white* precipitate of bismuth hydroxide, $Bi(OH)_3$, unaltered by excess of the reagent.

Allow this precipitate to settle, pour off the liquid as far as possible, and add *dilute hydrochloric acid* **drop by drop** till the $Bi(OH)_3$ is *just* redissolved. [This will give a solution of bismuth chloride, as nearly neutral as possible, for use in the next reaction].

(3) A solution of bismuth chloride (as nearly neutral as may be) if added to **a large excess of water** reacts with it to give a *white* precipitate of *bismuth oxychloride* (bismuthyl chloride), (BiO)Cl.

$$BiCl_3 + H_2O = (BiO)Cl + 2HCl.$$

*Note.*—A solution of bismuth nitrate reacts in a similar way with much water, but in that case the bismulthyl nitrate, $(BiO)(NO_3)$ itself is easily acted on further by more water—

$$2(BiO)(NO_3) + H_2O = (BiO) . O . Bi(OH)(NO_3) + H(NO_3),$$

and this still more 'basic' nitrate is the well-known 'bismuth subnitrate' used in medicine.

(4) Take two or three drops of **stannous chloride** solution and add **sodium (or potassium) hydroxide** solution until the precipitate (of stannous hydroxide) first formed is re-dissolved in excess of the alkali. Then *dilute with water* until the test-tube is nearly full and add **one drop** of the

bismuth-salt solution. A *black* precipitate, of *metallic bismuth* is formed.

*Note.*—This is another instance of *reduction*. The stannous hydroxide, $Sn(OH)_2$, dissolves in the alkali to form a stannite, e.g. $Sn(OK)_2$ or $K_2(SnO_2)$. This salt is a powerful reducing agent, combining with oxygen to produce the stannate, e.g. $K_2(SnO_3)$. The bismuth salt and the alkali yield bismuth hydroxide and this is reduced as follows :—

$$\left\{ \begin{array}{l} 2Bi(OH)_3 = 2Bi + 3H_2O + [3O], \\ 3K_2(SnO_2) + [3O] = 3K_2(SnO_3). \end{array} \right\}$$

## VIII.

## TIN.—Symbol **Sn** (*Stannum*); Atomic Weight **119.**

### **Divalent** *and* **Tetravalent.**

This metal forms two oxides and two corresponding series of salts, that is to say *there are two basic oxides of tin.* These oxides are, respectively, **stannous** oxide (black) $SnO$ and **stannic** oxide (white) $SnO_2$, the latter being commonly known as tin dioxide. The salts are derived from these oxides (in practice, from the corresponding hydroxides $Sn(OH)_2$ and $Sn(OH)_4$) by their reaction with acids, water being eliminated, in the usual way.

*Note.*—Neither of these oxides is exclusively basic in character, for though both of them (in the hydrated form at all events) will give salts with acids as stated, both will also dissolve in solutions of alkalis. The stannous hydroxide yields *stannites* and the stannic hydroxide *stannates*, e.g. $K_2(SnO_2)$ potassium stannite and $K_2(SnO_3)$ potassium stannate. We shall however be concerned, almost wholly, with the salts that they form with acids.

**Formulae of chief compounds :—**

| | | |
|---|---|---|
| **1. Stannous** | Oxide $SnO$ | Hydroxide $Sn(OH)_2$ |
| | Chloride $SnCl_2$ | Sulphide $SnS$ |
| **2. Stannic** | Oxide $SnO_2$ | Hydroxide $Sn(OH)_4$ |
| | Chloride $SnCl_4$ | Sulphide $SnS_2$ |

It will be observed that no formulae of nitrates or sulphates are given. This is because, although these salts *are* known, they are very unstable, being decomposed by water with formation of insoluble basic salts and, ultimately, the hydroxides.

**Properties of the metal.**—Tin is a white metal which melts at an even lower temperature (233°C) than bismuth. At ordinary temperatures it is malleable, but at about 200° it becomes exceedingly brittle and can easily be powdered. It is remarkable for the crackling sound that it emits when bent.

**Action of air (or oxygen).**—At ordinary temperatures tin suffers no change in air, but above its melting point it is readily oxidized to stannic oxide $SnO_2$.

**Action on water.**—*None.*

**Action of acids.**—Boiling **concentrated hydrochloric acid** is the *solvent* for tin. The metal dissolves readily, hydrogen being evolved and a solution of stannous chloride remaining. The dilute acid only dissolves the metal *very slowly.*

**Nitric acid,** when dilute enough, can dissolve the metal, yielding a solution that contains stannous nitrate and ammonium nitrate, without evolution of any gas :—

$$4Sn + 10H(NO_3) = 4Sn(NO_3)_2 + (NH_4)(NO_3) + 3H_2O.$$

This, however, is not the usual action of nitric acid on the metal. The acid (moderately diluted with water) acts as an oxidizing agent, converting the tin into '**metastannic acid,**' whose composition is represented by the formula $H_2SnO_3$ (i.e. $SnO_2 + H_2O$). This does not dissolve, but forms a *white powder.*

$$\left\{ \begin{array}{l} 4H(NO_3) = 2H_2O + 4NO + [6O] \\ 3Sn + [6O] + 3H_2O = 3H_2(SnO_3) \end{array} \right\}$$

**Sulphuric acid** when *dilute* dissolves tin very slowly, and the solution contains stannous sulphate. The *concentrated* acid, when hot, converts the metal into *stannic sulphate*, with evolution of sulphur dioxide

$$Sn + 4H_2(SO_4) = Sn(SO_4)_2 + 4H_2O + 2SO_2.$$

*Note.*—Aqua regia (see Note (ii), p. 21) is also a solvent for tin. The product is a solution of *stannic* chloride, $SnCl_4$. This compound is, when pure, a liquid, but it combines with water to give a crystalline hydrate, $SnCl_4 . 5H_2O$ which is used commercially.

## Reactions of Tin Salts in solution.

### 1. Stannous Salts ($Sn^{\cdot\cdot}$).

[Use a solution of stannous chloride].

(1) The solution, **acidified with dilute hydrochloric acid,** yields with **hydrogen sulphide** solution a *dark brown* (or *black*) precipitate of stannous sulphide, SnS.

Allow this precipitate to settle, pour off the liquid, add excess of *yellow ammonium sulphide* solution and warm gently. The precipitate is dissolved: *stannous sulphide is soluble in yellow ammonium sulphide solution.* [Contrast this with the behaviour of HgS, CuS and $Bi_2S_3$].

*Note.*—In this dissolution of the stannous sulphide two reactions occur. In the first place the yellow ammonium sulphide, whose formula may be taken as $(NH_4)_2S_2$, gives up part of its sulphur to the stannous sulphide, 'oxidizing' it to stannic sulphide :—

$$(NH_4)_2S_2 + SnS = (NH_4)_2S + SnS_2.$$

This is an "oxidation" because *the relative proportion of metal is decreased.* In the second place the stannic sulphide formed combines with ammonium sulphide to form the soluble salt ammonium sulphostannate :—

$$(NH_4)_2S + SnS_2 = (NH_4)_2(SnS_3).$$

If now the solution be *acidified* with dilute hydrochloric acid ammonium chloride is formed and sulphostannic acid itself is set free :—

$$(NH_4)_2(SnS_3) + 2HCl = 2(NH_4)Cl + H_2(SnS_3).$$

and this at once breaks up into $H_2S$, which is evolved as gas, and $SnS_2$ which forms a *yellow precipitate.*

(2) **Sodium (or potassium) hydroxide solution** (add this *gradually*) produces a *white* precipitate of *stannous hydroxide*, $Sn(OH)_2$.

Divide the precipitate and liquid between two test-tubes :—

(*a*) boil one portion—the precipitate *turns black*, being transformed gradually into crystalline stannous oxide, SnO.

(*b*) add to the other portion excess of the alkali. The precipitate is at once *dissolved.*

*Note.*—The solution contains the alkaline stannite. Its action as a reducing agent has been illustrated in test (4), pp. 29 and 30 above.

(3) If a solution of a stannous salt, acidified with dilute hydrochloric acid, be added gradually to a solution of **mercuric chloride** a *white* precipitate of mercurous chloride is first formed which, with more of the stannous solution, is converted into *grey* metallic mercury.

> *Note.*—This application of stannous chloride as a reducing agent has been explained in the Note on p. 24 above.

### 2. Stannic Salts ($Sn^{\cdot\cdot\cdot\cdot}$).

[Use a solution ot stannic chloride].

(1) The solution, **acidified with dilute hydrochloric acid,** yields with **hydrogen sulphide** solution a *yellow* precipitate of *stannic sulphide*, $SnS_2$.

> Allow this precipitate to settle, pour off the liquid, add excess of *yellow ammonium sulphide* solution and warm gently. The precipitate is immediately *dissolved: stannic sulphide is soluble in yellow ammonium sulphide solution* [see note under stannous sulphide above].

(2) **Ammonia solution** produces a *white gelatinous* precipitate of *stannic hydroxide*, $Sn(OH)_4$, which is insoluble in excess of the reagent.

(3) **Sodium (or potassium) Hydroxide solution** (add this *gradually*) produces a white gelatinous precipitate, $[Sn(OH)_4)]$, which is easily soluble in excess of the reagent, yielding a solution of the alkaline stannate :—

$$\begin{cases} SnCl_4 + 4K(OH) = Sn(OH)_4 + 4KCl \\ Sn(OH)_4 + 2K(OH) = K_2(SnO_3) + 2H_2O \end{cases}$$

### Reaction common to all salts of tin.

Metallic beads, on charcoal, (see Chapter VI) are given by all the tin salts and afford a further confirmatory test.

## IX.

## ARSENIC.—Symbol **As**; Atomic Weight **75**.

### **Trivalent** *and* **Pentavalent.**

This element not only forms two oxides,

**arsenious** oxide $As_4O_6$ [$As_2O_3$]
and **arsenic** oxide $As_2O_5$,

but also plays two parts, acting sometimes like a metal, but far more often as a non-metal. The oxide $As_4O_6$ can react with acids, behaving as though it were '$As_2O_3$' and yielding solutions in which the metallic radical $\mathbf{As}^{\cdots}$ may be recognized, e.g.

$$As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O.$$

The oxide $As_2O_5$ does not react with acids to form salts at all. On the contrary, it combines with water to form an acid, *arsenic acid*, $H_3AsO_4$ (a compound very like phosphoric acid $H_3PO_4$). *Arsenic oxide*, then, has only acidic properties.

Thus the only salts of arsenic as a metal are those in which it is trivalent. Pentavalent arsenic yields arsenic acid and the arsenates which will be discussed, under acid radicals, below. And even trivalent arsenic yields an acid also. Arsenious oxide is not only capable of reacting with some acids to form salts, but can in addition combine with water to form an acid, *arsenious acid*, that will react with bases to form salts, called *arsenites*. Thus arsenious oxide is both a basic oxide and an acidic oxide (or anhydride). Here we are concerned only with arsenic as a metallic radical.

**Properties of the element.**—Arsenic is a metallic-looking crystalline solid, dark steel-grey in colour, very brittle, and easily powdered. When heated it does not melt, but passes directly from solid to vapour. The vapour will re-condense upon a cooled surface, and the arsenic is then said to have been *sublimed*.

**Action of air (or oxygen).**—Arsenic is slowly oxidized on the surface when exposed to moist air, becoming darker in colour. Heated in air, or in oxygen, it takes fire and burns, forming dense white fumes of arsenious oxide ('*white arsenic*') $As_4O_6$. At the same time a powerful and unpleasant smell resembling that of garlic is perceptible. This however is not the smell of arsenious oxide, for that compound is odourless.

*Note.*—It should be observed that arsenic will not burn to the pentoxide. The arsenious oxide might, so far as composition goes, be represented by the formula $As_2O_3$, but its vapour is found to be nearly 198 times as dense as hydrogen so that its molecular weight must be 396 and its formula $As_4O_6$.

**Action on water.**—*None.*

**Action of acids.**—Hydrochloric acid does not attack the element. Both *nitric* and *sulphuric* acids will do so when they are *concentrated* and *hot*. In neither case, however, is an arsenic salt formed. The element is simply oxidized to the *pentoxide* which combines with the water formed to produce *arsenic acid*, while oxides of nitrogen are evolved in case of nitric acid and sulphur dioxide in that of sulphuric. The *element* arsenic then *does not yield salts* by the action of acids.

*Note.*—The reactions involved in these oxidations may be summarized as :—

$$\left.\begin{aligned} 2H(NO_3) &= H_2O + 2NO + [3O] \\ \text{or } H_2(SO_4) &= H_2O + SO_2 + [O] \end{aligned}\right\}$$

$$\left.\begin{aligned} 2As + [5O] &= As_2O_5 \\ As_2O_5 + 3H_2O &= 2H_3(AsO_4). \end{aligned}\right\}$$

**Formulae of chief compounds :—**

**Arsenious** Oxide $As_4O_6$ ($As_2O_3$) Hydroxide $As(OH)_3$ (arsenious acid)

Chloride $AsCl_3$ Sulphide $As_2S_3$.

N.B.—**Arsenic compounds are very poisonous. They should be handled carefully and in small quantities, and the fumes should not be inhaled.**

## Reactions of Arsenious Salts in Solution.

[Use a solution of arsenic chloride.]

(1) The solution, **acidified with dilute hydrochloric acid,** yields with **hydrogen sulphide** solution a *yellow* precipitate of *arsenic sulphide*, $As_2S_3$.

Allow this precipitate to settle, pour off the liquid, add excess of *yellow ammonium sulphide* solution and warm gently. The precipitate is immediately dissolved: *sulphide of arsenic is soluble in yellow ammonium sulphide solution.*

*Notes.*—(i) The sulphide $As_2S_3$ here takes sulphur from the $(NH_4)_2S_2$ to become $As_2S_5$ which combines with the ammonium sulphide forming *ammonium sulpharsenate* which is a soluble salt:—

$$\begin{cases} As_2S_3 + 2(NH_4)_2S_2 = As_2S_5 + 2(NH_4)_2S \\ As_2S_5 + 3(NH_4)_2S = 2(NH_4)_3(AsS_4). \end{cases}$$

(ii) It will be observed that this sulphide is, in colour and in behaviour towards the ammonium sulphide solution, indistinguishable from stannic sulphide. Hence *we shall next apply that test used as No. (2) for stannic salts.*

(2) **Ammonia solution** produces **no precipitate** with a solution of an arsenic salt.

*Notice the difference between this case and that of stannic salts.*

*Note.*—Here is an example of the value which a *negative* result *may* possess in chemical analysis. A yellow sulphide, produced in presence of dilute hydrochloric acid and dissolved by yellow ammonium sulphide, might be either $SnS_2$ or $As_2S_3$. The behaviour of the original solution with ammonia will indicate which it is. Of course such evidence must be supplemented by some additional tests, such as those which follow.

(3) **Reinsch's Test.**—A strip of **clean** bright **copper foil** is boiled, in a large test-tube with 10 to 15 ccs. of a mixture of **equal volumes of concentrated hydrochloric acid and water.** Then **one drop** of the solution to be tested is added, and the **boiling is continued for several minutes.** The liquid is poured away, and the strip is washed with water, turned out upon a filter paper and carefully dried. If arsenic is present the slip will have become coated with this element, and will have acquired an extremely characteristic *purple-grey colour.*

[Notice this colour very carefully. Other metallic elements may coat a strip of copper, but none gives anything like this shade.]

(4) To the solution of an arsenious salt add *a few drops* of **dilute hydrochloric acid** and then **one drop of copper sulphate** solution. Then add a solution of **sodium (or potassium) hydroxide** *drop by drop* (shaking after each drop). As the mixture becomes neutral a *green precipitate* of copper arsenite, $Cu_3(AsO_3)_2$, separates. This dissolves, on

adding excess of the alkali, to a *clear blue solution.* When this blue solution is boiled, a *red precipitate* of cuprous oxide, $Cu_2O$, gradually comes down.

*Note.*—The blue solution contains cupric hydroxide, $Cu(OH)_2$ held in solution by alkali and alkaline arsenite. The arsenite acts as a *reducing agent* thus :—

$$K_3(AsO_3) + H_2O = K_3(AsO_4) + [2H]$$
$$2Cu(OH)_2 + [2H] = 3H_2O + Cu_2O.$$

being itself oxidized into the arsenate.

The volatilization and sublimation of many arsenic compounds when heated by themselves is very characteristic (see Chapter VI).

## X.

## ANTIMONY.—Symbol **Sb** (*Stibium*); Atomic Weight **120.**

### Trivalent and Pentavalent.

This element forms three oxides, of which the formulae are $Sb_4O_6(Sb_2O_3)$, $Sb_2O_4$ and $Sb_2O_5$, respectively. The first-named is the only basic oxide and the antimony salts are derived from it, e. g.

$$Sb_2O_3 + 6HCl = 2SbCl_3 + 3H_2O.$$

The oxide $Sb_2O_5$ is an acidic oxide, like $P_2O_5$ and $As_2O_5$, yielding antimonic acid comparable with arsenic and phosphoric acids.

We shall consider here only the compounds in which antimony is trivalent.

**Formulae of chief compounds :—**

| | |
|---|---|
| Oxide $Sb_4O_6$ ($Sb_2O_3$) | Hydroxide $Sb(OH)_3$ |
| Chloride $SbCl_3$ | Sulphide $Sb_2S_3$. |

Just as bismuth chloride, $BiCl_3$, reacts with much water to form bismuth oxychloride, (BiO)Cl (see p. 29 above), so also, in a similar manner, does antimony chloride, $SbCl_3$ yield antimony oxychloride, (SbO)Cl.

Moreover, other compounds are also known in which the trivalent antimony, $Sb^{\cdot\cdot\cdot}$, by associating itself with a divalent oxygen atom, $O''$, becomes the *monovalent radical* $(SbO)^{\cdot}$ to which the name '*antimonyl*' has been given. One of the most important antimony derivatives is **tartar emetic**, which is derived from the dibasic acid, tartaric acid, $H_2(C_4H_4O_6)$, by the replacement of one of the hydrogen atoms by potassium and the other one by 'antimonyl,' thus:—$K(SbO)(C_4H_4O_6)$. These 'antimonyl' salts, however, give, in solution, the antimony $(Sb''')$ reactions described below.

**Properties of the metal.**—Antimony is bluish-white, hard and brittle. It melts at (630°C) a much higher temperature than lead, bismuth or tin, and is crystalline.

**Action of air (or oxygen).**—Antimony is not affected by oxygen at ordinary temperatures but, when heated in the air, it burns very readily, giving off dense white fumes of the oxide, $Sb_4O_6$.

*Note.*—This combustibility of antimony at high temperatures can be illustrated in a striking manner by melting a fragment of the metal on charcoal (in the blow-pipe flame) and allowing the drop of molten metal to fall upon a sheet of white paper. The burning globule splits up into a number of smaller ones which, as they run athwart the paper, scorch upon it a series of marks that form parts of characteristic curves.

**Action on water.**—Antimony does not act upon water at ordinary temperatures, but, at a red heat, the metal decomposes *steam* with the formation of the oxide $Sb_4O_6$ and evolution of hydrogen.

**Action of acids.**—Neither hydrochloric nor sulphuric acid will dissolve the metal. It is *attacked* by *nitric acid* (suitably diluted with water), being oxidized to $Sb_4O_6$ and $Sb_2O_5$, while oxides of nitrogen are evolved. The oxides of antimony formed remain undissolved.

To **dissolve** antimony, the simplest plan is to boil it with a mixture of **dilute nitric and tartaric acids.** The nitric acid oxidizes the metal and the tartaric acid dissolves the oxide formed, giving antimonyl tartrate.

*Note.*—Another way to dissolve antimony is to use aqua regia and to evaporate off the excess of acid leaving a solution of antimony chloride $SbCl_3$.

## Reactions of antimony salts in solution.

[Use a solution of antimony chloride].

(1) The solution **acidified with dilute hydrochloric acid,** yields with **hydrogen sulphide solution** an *orange* precipitate of *antimony sulphide* $Sb_2S_3$.

> Allow the precipitate to settle, pour off the liquid, add excess of *yellow ammonium sulphide solution* and warm gently. The precipitate is quickly dissolved; *antimony sulphide is soluble in yellow ammonium sulphide solution* forming a solution of ammonium sulphantimonate $(NH_4)_3(SbS_4)$.
>
> [*Notice carefully the colour of the* $Sb_2S_3$ *and learn to distinguish it from the bright yellow of* $SnS_2$ *and* $As_2S_3$].

(2) **Ammonia solution** produces a *white* precipitate of *antimony hydroxide*, $Sb(OH)_3$. Let the precipitate settle, pour away the liquid, and add dilute hydrochloric acid *drop by drop* until the precipitate is just dissolved. This will give a solution, as nearly neutral as possible, of antimony chloride for the next test.

(3) A solution of **antimony chloride** (prepared as above) poured into **much water,** yields a *white* precipitate of *antimony oxychloride* (antimonyl chloride), (SbO)Cl.

$$SbCl_3 + H_2O = (SbO)Cl + 2HCl.$$

[Compare with reaction (3) of bismuth.]

(4) Into a dilute solution of an antimony salt, acidified with hydrochloric acid, put a piece of **granulated zinc.** Then take a clean straight piece of **platinum wire** (or foil) and place it in the liquid so that one end of it touches the zinc. The platinum will rapidily become coated with a *perfectly black* deposit of antimony.

> *Note.*—The point of this test is that the antimony is deposited *upon the platinum* and that its colour, when so deposited, is *dead black.*

The production of antimony beads on charcoal, and the partial combustion of the metal to white fumes of the oxide, is also characteristic (see Chapter VI).

## XI.

### CADMIUM.—Symbol **Cd** ; Atomic Weight **112·5.**

### Divalent.

**Formulae of chief compounds**:—

| | | |
|---|---|---|
| Oxide CdO | Hydroxide $Cd(OH)_2$ | Chloride $CdCl_2$ |
| Nitrate $Cd(NO_3)_2$ | Sulphate $Cd(SO_4)$ | Sulphide CdS. |

**Properties of the metal.**—Cadmium is a white metal. It is malleable, and not very hard. It melts easily (at 320°C.) and boils at a low enough temperature to be sublimed in a glass tube. When bent it crackles like tin.

**Action of air (or oxygen).**—No action occurs at ordinary temperatures, but, when strongly heated, the metal burns, giving *brown* fumes of cadmium oxide, CdO.

**Action on water.**—The heated metal reacts with *steam* to form the oxide and hydrogen.

**Action of acids.**—The metal is **dissolved** by dilute hydrochloric or dilute sulphuric acid with evolution of hydrogen and formation of the chloride, $CdCl_2$, and sulphate, $Cd(SO_4)$, solutions respectively. Dilute nitric acid attacks the metal even more easily, forming cadmium nitrate, $Cd(NO_3)_2$, solution and evolving oxides of nitrogen.

### Reactions of Cadmium Salts in Solution.

[Use a solution of cadmium sulphate or nitrate.]

(1) The solution, **acidified with dilute hydrochloric acid,** yields with **hydrogen sulphide solution** a *yellow* precipitate of *cadmium sulphide*, CdS.

> Allow this precipitate to settle, pour off the liquid, add excess of *yellow ammonium sulphide* solution and warm gently. The precipitate does not dissolve; *cadmium sulphide is insoluble in yellow ammonium sulphide solution.*
>
> *Note.*—Contrast the behaviour of CdS with that of the other two yellow sulphides, stannic sulphide $SnS_2$ and arsenic sulphide $As_2S_3$.

(2) **Ammonia solution** (add this *gradually*) produces a *white* gelatinous precipitate of *cadmium hydroxide*, $Cd(OH)_2$, which is very easily soluble in excess of the precipitant. If to this clear solution of cadmium hydroxide in ammonia a solution of hydrogen sulphide be added, the yellow cadmium sulphide is again precipitated, but this time in a gelatinous, semi-transparent form.

The formation of a brown film when cadmium salts are heated, with sodium carbonate, on charcoal in the reducing flame is very characteristic (see Chapter VI).

## XII.

### GROUP II.

The metallic radicals $\mathbf{Hg}^{\cdot\cdot}$, $\mathbf{Cu}^{\cdot\cdot}$, $\mathbf{Bi}^{\cdot\cdot\cdot}$, $\mathbf{Sn}^{\cdot\cdot}$, $\mathbf{Sn}^{\cdot\cdot\cdot\cdot}$, $\mathbf{As}^{\cdot\cdot\cdot}$, $\mathbf{Cd}^{\cdot\cdot}$ and $\mathbf{Sb}^{\cdot\cdot\cdot}$ constitute a second '**group**,' every member of which is characterized by the fact that its salts, in solution, *when acidified with dilute hydrochloric acid*, give *no precipitate* (Group I) *but when further treated with hydrogen sulphide solution* yield a *precipitate* of the sulphide ($HgS$, $CuS$, $Bi_2S_3$, $SnS$, $SnS_2$ $As_2S_3$, $CdS$ or $Sb_2S_3$). In short, *the sulphides of all these radicals are insoluble in cold dilute hydrochloric acid.*

**(a)** Two of these sulphides are unmistakeable. That of **mercury** is black, like some of the others, but its formation is preceded, when hydrogen sulphide is added gradually, by that of a *white* sulphochloride and this turns *yellow*, then *brown*, and *finally black* (see p. 23). That of **antimony** has a *reddish orange* colour, perfectly distinct, alike from the yellow of $SnS_2$, $As_2S_3$ or $CdS$, and from the dark brown (or black) of $CuS$, $Bi_2S_3$ or $SnS$. Whenever, then, the group precipitate is such as to indicate the presence of a mercuric or of an antimony salt apply at once to fresh portions of the original solution two or more of the confirmatory tests for mercuric salts (p. 23), or for those of antimony (p. 39) given above.

**(b)** The remaining radicals then fall into two divisions, viz. those whose sulphides are *dark brown* (*or black*), ($Cu^{\cdot\cdot}$, $Bi^{\cdot\cdot\cdot}$, $Sn^{\cdot\cdot}$) and those whose sulphides are *yellow*, ($Sn^{\cdot\cdot\cdot\cdot}$, $As^{\cdot\cdot\cdot}$, $Cd^{\cdot\cdot}$).

The further distinction between these is easily made as follows:—

(**c**) Examine the solubility of the precipitate in yellow ammonium sulphide.

| | | |
|---|---|---|
| *Dark coloured sulphides* | $CuS$ | insoluble |
| | $Bi_2S_3$ | |
| | $SnS$ | *soluble* |
| *Yellow sulphides* | $SnS_2$ | *soluble* |
| | $As_2S_3$ | |
| | $CdS$ | insoluble. |

(i) In case the *black (or dark-brown)* sulphide is *soluble in ammonium sulphide* we must have to do with a **stannous** salt. Acidify the solution (of $SnS$ in $(NH_4)_2S_2$, see p. 32) with dilute hydrochloric acid and obtain the yellow precipitate of $SnS_2$. Then apply to more of the original solution confirmatory tests for $Sn^{\cdot\cdot}$.

(ii) In case the *black* (*or dark brown*) sulphide is *insoluble in ammonium sulphide* it may be *either* **$CuS$** *or* **$Bi_2S_3$**. Which, of these, can be ascertained by testing a fresh portion of the original solution with ammonia, when the reaction characteristic of *either* **copper** salts (p. 27) *or* **bismuth** salts (p. 29) must be observed. Whichever of these be indicated, apply further confirmatory tests as given above.

(iii) In case the *yellow* sulphide is *insoluble in ammonium sulphide* it must be that of **cadmium.** Apply to a fresh portion of the original solution a confirmatory test for $Cd^{\cdot\cdot}$ (p. 41).

(iv) Finally, in case the *yellow* sulphide is *soluble in ammonium sulphide* it must be either **$SnS_2$** or **$As_2S_3$**. Once again the reaction obtained on treating a fresh portion of the original solution with ammonia will decide which, **stannic** salts giving a precipitate (p. 33) and **arsenic** salts no precipitate (p. 36) with this reagent. Whichever be indicated apply further confirmatory tests as given above.

ADDENDUM.—**Note on reactions which may occur when hydrogen sulphide is added to the acidified solutions of certain salts.**

There are certain cases in which the addition of hydrogen sulphide solution to a solution already containing dilute hydrochloric acid gives rise to a reaction which is not one of those described above. These cases may be classed under two headings.

(*a*) **a change of colour** occurs in the test-solution, accompanied or followed by the formation of a 'thin' **white** precipitate.

(*b*) there is immediate formation of a **white** precipitate without any noticeable change of colour in the liquid.

In all these cases *the white precipitate*, which is usually so finely divided as to make the liquid appear milky, and does not settle on standing, *consists of sulphur*. It has been produced by the oxidation of the hydrogen sulphide :—

$$\mathbf{H_2S + [O] = H_2O + S}$$

and its appearance indicates the presence of some substance capable of thus oxidizing that compound.

The number of such substances is considerable, but we shall here notice only a few instances :

(i) The test-solution was originally *yellow or brown* and, on addition of hydrogen sulphide, becomes *colourless* or *very pale green*, with simultaneous separation of finely-divided sulphur. The solution contains a *ferric* salt which is reduced to the ferrous state (see below, under Iron).

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

(ii) The test-solution was originally *orange* and, on addition of hydrogen sulphide, becomes *green* with gradual, subsequent, separation of finely-divided sulphur.

The solution contains a *chromate* which on acidification has given *chromic acid* (see this, Chapter III). This can act as an oxidizing agent being reduced, in presence of hydrochloric acid, to chromium chloride :—

$$\left\{\begin{array}{c} 2H_2(CrO_4) + 6HCl = 2CrCl_3 + 5H_2O + [3O] \\ 3H_2S + [3O] = 3H_2O + 3S. \end{array}\right.$$

The chromium chloride solution is green.

If either of these two cases should arise *add an excess of hydrogen sulphide solution* to make sure that no member of Group II. is present—for the hydrogen sulphide *at first* introduced will have been destroyed by the oxidizing agent—and, if no other reaction than those described takes place, infer the *absence* of Group II. and the *presence* of either a ferric salt or a chromate. Then proceed to test a fresh portion of the original solution for Group III., and so on, as described in the succeeding pages.

(iii) The test-solution does not show any distinct colour-change, but gives at once a *white* precipitate (of sulphur) which remains white when excess of hydrogen sulphide solution is added. This is probably due to the presence of either a *sulphite* or a *nitrite* [or a *hypochlorite*].

Sulphites on acidification give sulphur dioxide and this reacts with hydrogen sulphide as follows:—

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

while nitrites give nitrous acid which reacts thus:—

$$\begin{cases} 2H(NO_2) = H_2O + 2NO + [O] \\ H_2S + [O] = H_2O + S. \end{cases}$$

In either case the addition of the dilute hydrochloric acid will have produced an evolution of either $SO_2$ or nitrous fumes which should have been observed. It is only necessary to boil well the solution containing the dilute hydrochloric acid in order to expel the sulphur dioxide or the nitrous acid, then cool, and *then* make the test for Group II.

## XIII.

## METALS OF GROUP III.

The metallic radicals which are not precipitated either by dilute hydrochloric acid (Group I) or by hydrogen sulphide in the presence of dilute hydrochloric acid (Group II) include the following:—iron, nickel, cobalt, manganese, zinc, aluminium, chromium, barium, strontium, calcium, magnesium, (ammonium), potassium, and sodium.

Of these, the seven first named are distinguished from the remaining seven by the fact that **hydrogen sulphide, in the presence of ammonium chloride and ammonia,** produces with solutions of their salts characteristic **precipitates.**

Hydrogen sulphide and ammonia produce, of course, *ammonium sulphide*:—

$$H_2S + 2NH_3 = (NH_4)_2S$$

and this constitutes the 'group-reagent' for these seven metallic radicals. It is necessary, however, that it should be made in the tube where it is to be used, for ammonium sulphide solution will not keep, and the so-called 'ammonium sulphide' of which we have made use as a solvent in Group II is not really the compound $(NH_4)_2S$, but a mixture of this with polysulphides of ammonium.

Hence the 'group test' is made by adding

(1) *an equal volume of ammonium chloride solution*,

(2) *ammonia solution till the liquid has an alkaline reaction*,

and (3) *hydrogen sulphide solution*,

to a portion of the original solution.

*Notes.*—(i) The presence of ammonium chloride is absolutely necessary to the successful use of ammonium sulphide as a group-reagent, for, without it, *magnesium* salts would also give a precipitate here, and this would complicate the group.

(ii) It frequently happens that when **ammonia** solution is added to the test-solution a **precipitate** is produced. **This does not interfere with the group-test. The hydrogen sulphide must be added, and the FINAL result observed,** before any conclusions are drawn. Impor

We shall now proceed to a study of the elements *iron*, *nickel*, *cobalt*, *manganese*, *zinc*, *aluminium* and *chromium* (Group III).

## IRON.—Symbol **Fe** (*Ferrum*); Atomic Weight **56.**

### Divalent and Trivalent.

This metal forms three oxides, two of which, FeO, ferrous oxide, and $Fe_2O_3$, ferric oxide (the common red oxide), are ordinary *basic* oxides yielding corresponding series of salts by their reactions with acids. The third oxide, $Fe_3O_4$, reacts with acids to form both ferrous and ferric salts simultaneously, thus:—

$$FeO + 2HCl = H_2O + FeCl_2 \ (\textit{ferrous})$$
$$Fe_2O_3 + 6HCl = 3H_2O + 2FeCl_3 \ (\textit{ferric})$$
$$Fe_3O_4 + 8HCl = 4H_2O + FeCl_2 + 2FeCl_3 \ (\textit{ferrous AND ferric}).$$

Hence the oxide $Fe_3O_4$ is commonly known as *ferroso-ferric oxide.*

**Formulae of chief compounds:—**

| | | |
|---|---|---|
| **Ferrous** | (Oxide FeO) | Hydroxide $Fe(OH)_2$ |
| | Sulphide FeS | Sulphate $Fe(SO_4)$ |
| | Chloride $FeCl_2$ | Carbonate $Fe(CO_3)$ |

**Ferric** Oxide $Fe_2O_3$ Hydroxide $Fe(OH)_3$
Sulphate $Fe_2(SO_4)_3$ Chloride $FeCl_3$
Nitrate $Fe(NO_3)_3$.

**Properties of the metal.**—Iron is a hard tough metal, with a very high melting point. It is grey-white in colour, and capable of taking a high polish. When pure (*wrought iron*) it is malleable, but its compounds with carbon (e.g. in *cast iron* and *steel*) are more or less brittle.

**Action of air (or oxygen).**—Iron *rusts* in moist air, the rust being ferric hydroxide, $Fe(OH)_3$. In dry air it is not affected. When heated in air, iron is superficially oxidized, the oxide formed being $Fe_3O_4$. This same oxide, mixed with ferric oxide, is formed when iron is made to burn in oxygen.

**Action on water.**—In the presence of air iron *rusts* in contact with water (see above). Red-hot iron decomposes *steam*, combining with the oxygen to form the black oxide, $Fe_3O_4$, and liberating the hydrogen.

**Action of acids.**—Iron is **dissolved** by *hydrochloric acid* and by *dilute sulphuric acid*, with liberation of hydrogen and formation of **ferrous** chloride and **ferrous** sulphate solutions respectively:—

$$Fe + H_2(SO_4) = Fe(SO_4) + H_2$$
$$Fe + 2HCl = FeCl_2 + H_2.$$

*Pure strong nitric acid* does not attack iron at all ('*passive*' iron). The metal is acted upon by nitric acid (suitably diluted with water) with the formation of **ferric** nitrate solution and evolution of oxides of nitrogen.

*Note.*—Ferrous nitrate (with ammonium nitrate) solution can be got by the action of cold very dilute nitric acid upon iron.

$$4Fe + 10H(NO_3) = 4Fe(NO_3)_2 + (NH_4)(NO_3) + 3H_2O.$$

Stronger nitric acid at once oxidizes the ferrous to the ferric salt:—

$$2H(NO_3) = H_2O + 2NO + 3[O]$$
$$2Fe(NO_3)_2 + 2H(NO_3) + [O] = 2Fe(NO_3)_3 + H_2O.$$

Iron is acted upon by *hot concentrated sulphuric acid* with the evolution of sulphur dioxide and the formation of **ferric** sulphate (compare other metals).

## Reactions of Ferrous Salts in Solution.

[Use a freshly-made solution of ferrous sulphate in cold water.]

(1) The solution, treated with an equal volume of **ammonium chloride solution**, then with **ammonia solution** (TILL ALKALINE) and then with **hydrogen sulphide solution**, gives a *black* precipitate of *ferrous sulphide*, FeS.

(2) **Sodium (or potassium) hydroxide solution**, when added to a solution of a PURE FERROUS SALT, gives a *white* precipitate of *ferrous hydroxide*, $Fe(OH)_2$, but this compound *absorbs oxygen very rapidly from the air and becomes dirty green. Usually*, the precipitate is dirty green from the outset owing to presence of ferric salt in the ferrous solution. The precipitate is insoluble in excess of alkali, and if the contents of the tube be shaken and allowed to stand awhile, a reddish brown film (rust) is formed on the top. This is due to the oxidation of ferrous to ferric hydroxide.

(3) **Potassium Ferricyanide**, $K_3[Fe(CN)_6]$, **solution** yields a **dark blue** precipitate of *ferrous ferricyanide*, $Fe_3[Fe(CN)_6]_2$—*Turnbull's Blue.*

(4) **Potassium Ferrocyanide**, $K_4[Fe(CN)_6]$, **solution** yields with a PURE FERROUS SALT solution a *white* precipitate, but *the precipitate actually obtained is always more or less blue*, owing to the presence of ferric salt produced by the oxidizing action of the air upon solutions of ferrous salts.

*Note.*—The precipitate given by ferrocyanide and a ferrous salt has **never that dark blue** colour characteristic of the precipitate obtained with ferricyanide.

## Reactions of Ferric Salts in Solution.

[Use a solution of ferric chloride].

(1) The solution, treated with an equal volume of **ammonium chloride solution**, then with **ammonia solution** (TILL ALKALINE), and then with **hydrogen sulphide solution**, yields a *black* precipitate of *ferrous sulphide*, FeS.

*Note.*—The addition of ammonia here precipitates ferric hydroxide, $Fe(OH)_3$, as a reddish-brown gelatinous precipitate. When the $H_2S$ is added this reacts as follows:—

$$2Fe(OH)_3 + 3H_2S = 2FeS + 6H_2O + S,$$

*the hydrogen sulphide acting as a reducing agent.*

(2) **Sodium (or potassium) hydroxide solution** gives a *reddish-brown* precipitate of *ferric hydroxide*, $Fe(OH)_3$.

(3) **Potassium Ferricyanide solution** gives **no precipitate** with ferric salts, but merely a *brown solution.*

(4) **Potassium Ferrocyanide solution** gives a **dark blue** precipitate of *ferric ferrocyanide*, $Fe_4[Fe(CN)_6]_3$—*Prussian Blue.*

(5) **Potassium Sulphocyanide** (Thiocyanate) **solution** gives no precipitate, but *a blood-red colouration.*

> *Notes.*—(i) Compare and contrast the reactions of ferrous and ferric salts with potassium ferrocyanide and ferricyanide respectively.
>
> (ii) Remember that no ferrous solution is ever really free from traces at all events of ferric salt, and therefore that *the only final test for a ferrous salt is the reaction with potassium ferricyanide.*

**Conversion of ferrous into ferric compounds, and vice-versa.**—The relation of ferrous to ferric salts is precisely like that of stannous to stannic salts. *The change from the ferrous to the ferric state is accompanied* (*like all changes of -ous to -ic salts*) *by a decrease in the relative proportion of the metal to the rest of the compound.* This decrease may either come about without change in the valency of the metal, as in the cases of mercury and copper above, or it may arise from a change of valency as when the divalent tin of stannous chloride ($SnCl_2$) is converted into the tetravalent tin of stannic ($SnCl_4$). *In the case of iron there is a change from the divalent to the trivalent condition.* Divalent iron becomes trivalent when it is oxidized: trivalent iron becomes divalent when it is reduced.

The oxidizing agent most commonly used to convert ferrous into ferric salts is nitric acid. When nitric acid acts as an oxidizing agent it is decomposed according to the scheme:—

$$2H(NO_3) = H_2O + 2NO + 3[O]$$

and the oxygen here represented as 'nascent' will effect the required oxidation, in presence of a sufficiency of the acid of the salt. Thus ferrous chloride, in the presence of hydrochloric acid, yields ferric chloride:—

$$2FeCl_2 + 2HCl + [O] = 2FeCl_3 + H_2O$$

and in this way it is made evident that the conversion of ferrous into ferric chloride is *really an oxidation.*

The most common instance of the reduction of ferrous to ferric salts is afforded by the behaviour of ferric solutions when tested (for Group II) with hydrogen sulphide in the presence of dilute hydrochloric acid, for, owing to the reduction of ferric to ferrous salt :—

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$$

the yellow or brown colour of the ferric solution disappears, and the solution becomes almost colourless (very pale green). At the same time a white turbidity, due to the separation of sulphur, is seen.

The colouration of the borax bead and the reduction to the metallic state on charcoal are characteristic reactions of iron compounds (see Chapter VI).

## XIV.

### NICKEL.—Symbol **Ni**; Atomic Weight, **58·7**.

### Divalent.

**Formulae of chief compounds :—**

| | | |
|---|---|---|
| Oxide $NiO$ | Hydroxide $Ni(OH)_2$ | Sulphide $NiS$ |
| Sulphate $Ni(SO_4)$ | Chloride $NiCl_2$ | Nitrate $Ni(NO_3)_2$ |

**Properties of the metal.**—Nickel is a white metal which very much resembles iron. It has a very high melting point.

**Action of air (or oxygen).**—At ordinary temperatures nickel does not rust in air. When heated to redness in air, the metal is superfically oxidized to nickel oxide, NiO.

**Action on water.**—Red-hot nickel decomposes steam slowly, combining with the oxygen to form NiO, and liberating the hydrogen.

**Action of Acids.**—Dilute hydrochloric and sulphuric acids act upon the metal liberating hydrogen and forming solutions of the chloride and sulphate respectively. Nitric acid (suitably diluted with water) readily dissolves the metal, forming a solution of the nitrate, with evolution of nitric oxide. Pure strong nitric acid renders nickel 'passive' just as it does iron.

### Reactions of Nickel Salts in Solution.

[Use a solution of nickel sulphate].

(1) The solution, treated with an equal volume of **ammonium chloride solution,** then with **ammonia solution** (TILL ALKALINE) and then with **hydrogen sulphide solution,** gives a *black* precipitate of *nickel sulphide*, NiS.

(2) **Sodium (or potassium) hydroxide solution** gives a *pale apple-green* precipitate of *nickel hydroxide*, $Ni(OH)_2$, *which does not darken or change in any way when shaken with air.*

The nickel borax bead is particularly characteristic (see Chapter VI).

## XV.

### COBALT.—Symbol **Co**; Atomic Weight, **59.**

**Divalent.**

**Formulae of chief compounds:—**

| | | |
|---|---|---|
| Oxide CoO | Hydroxide $Co(OH)_2$ | Sulphide CoS |
| Sulphate $Co(SO_4)$ | Chloride $CoCl_2$ | Nitrate $Co(NO_3)_2$. |

**Properties of the metal.**—Cobalt resembles nickel very closely.

**Action of air (or oxygen).**—The metal is stable at ordinary temperatures in air, but undergoes oxidation at a red heat.

**Action on water.**—Cobalt resembles nickel in its action on water.

**Action of Acids.**—Here again the behaviour of cobalt is closely analogous to that of nickel, but it is rather more easily attacked by the various acids and it does not become 'passive' with concentrated nitric acid.

### Reactions of Cobalt Salts in Solution.

[Use a solution of cobalt nitrate].

(1) The solution, treated with an equal volume of **ammonium chloride solution**, then with **ammonia solution** (TILL ALKALINE) and then with **hydrogen sulphide solution**, gives a *black* precipitate of *cobalt sulphide*, CoS.

(2) **Sodium (or potassium) hydroxide solution** gives a *blue* precipitate of a *basic salt*, e.g.

$$Co(NO_3)_2 + Na(OH) = Co(OH)(NO_3) + Na(NO_3).$$

When more of the alkali is added and the mixture is gently warmed, the basic salt is converted into pink cobalt hydroxide, $Co(OH)_2$.

*Note.*—If the solution containing the pink cobalt hydroxide be further heated in contact with the air, the precipitate darkens, being oxidized gradually to cobaltic hydroxide, $Co(OH)_3$.

The cobalt borax head is particularly characteristic (see Chapter VI).

## XVI.

### MANGANESE.—Symbol **Mn**; Atomic Weight, **55**.

In its *salts* Manganese is **divalent.**

This element forms many oxides. The common basic oxide is MnO. Of the other oxides, the well-known manganese dioxide, $MnO_2$, is a peroxide, yielding the salts of MnO, when it does react with acids, together with oxygen or the product of the action of oxygen upon the acid, e.g.

$$MnO_2 + H_2(SO_4) = Mn(SO_4) + H_2O + [O.]$$
$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

Intermediate between MnO and $MnO_2$, and related to them in the same way as red lead is related to PbO and $PbO_2$ (see p. 16), is an oxide $Mn_3O_4$ which occurs naturally, and is also formed when either of the other oxides is heated to redness in air.

The higher oxides are the anhydrides of acids, $MnO_3$ yielding $H_2(MnO_4)$, manganic acid (and the manganates) and $Mn_2O_7$ giving $H(MnO_4)$, permanganic acid (and the permanganates). These will be dealt with later, under *acids*.

**Formulae of chief compounds (divalent manganese):—**

| | | |
|---|---|---|
| Oxide $MnO$ | Hydroxide $Mn(OH)_2$ | Sulphide $MnS$. |
| Sulphate $Mn(SO_4)$ | Chloride $MnCl_2$ | Nitrate $Mn(NO_3)_2$. |

**Properties of the metal.**—Manganese is a pinkish-white metal which is hard and brittle. It has an extremely high melting point.

**Action of air (or oxygen).**—The pure metal is so oxidizable that it has to be kept under paraffin oil. As usually prepared, the metal contains iron and carbon, and can then be kept in air.

**Action on water.**—The pure metal decomposes water with the evolution of hydrogen and the formation of manganese hydroxide, but, here again, the cast metal (containing iron and carbon) is much less reactive.

**Action of Acids.**—All dilute acids attack manganese. Dilute hydrochloric and sulphuric acids form solutions of $MnCl_2$ and $Mn(SO_4)$ respectively, with evolution of hydrogen. Nitric acid (suitably diluted with water) yields a solution of the nitrate, $Mn(NO_3)_2$, with evolution of oxides of nitrogen.

## Reactions of Manganese Salts in Solution.

[Use a solution of manganese sulphate or chloride].

(1) The solution, treated with an equal volume of **ammonium chloride solution**, then with **ammonia solution** (TILL ALKALINE) and then with **hydrogen sulphide solution**, gives a *pink* precipitate of (hydrated) *manganese sulphide*, $MnS(+\text{aq.})$.

(2) **Sodium (or potassium) hydroxide solution** gives a *white* precipitate of *manganese hydroxide*, $Mn(OH)_2$, which is *insoluble in excess of the alkali, and, when shaken with air,*

*darkens in colour*, absorbing oxygen to form (hydrated) manganese dioxide :—

$$Mn(OH)_2 + O = MnO(OH)_2$$

the manganese becoming tetravalent.

(3) A *small* quantity of a *solid* manganese salt is dissolved in about 20 cc. of dilute nitric acid and the solution is *boiled.* Then *a very small quantity of red lead* is added and the boiling is continued for a few moments. On allowing the lead dioxide formed (see p. 19) to settle, the solution is seen to have a bright purple-red colour. This is attributed to the formation of permanganic acid ($HMnO_4$), through the oxidizing action of the lead dioxide.

The colouration of the borax bead by manganese compounds (see Chapter VI) and the formation of manganates by fusion with alkali carbonates and oxidizing agents (see Permanganic Acid, Chapter IV) afford further characteristic tests for manganese.

## XVII.

### ZINC.—Symbol **Zn** ; Atomic Weight, **65·5.**

### Divalent.

**Formulae of chief compounds :—**

| | |
|---|---|
| Oxide $ZnO$ | Hydroxide $Zn(OH)_2$ |
| Sulphide $ZnS$ | Sulphate $Zn(SO_4)$ |
| Chloride $ZnCl_2$ | Nitrate $Zn(NO_3)_2$ |

Carbonate $Zn(CO_3)$.

**Properties of the metal.**—Zinc is a bluish white metal, fairly hard, and easily fusible (melting point 420°C.). It boils at a high temperature (940°C.) and can be distilled. At just over 200° it becomes brittle so that it can be powdered in a mortar, but a little below this (100°—150°) it is both malleable and ductile.

**Action of air (or oxygen).**—At ordinary temperatures zinc only undergoes slight superficial oxidation. When sufficiently heated it burns with a bright flame, forming the oxide, $ZnO$ ('Zinc White'). This oxide is yellow while hot and becomes white again on cooling.

**Action on water.**—At ordinary temperatures zinc does not attack water. At a red heat it decomposes steam, zinc oxide being formed and hydrogen liberated.

**Action of Acids.**—The pure metal is very slowly attacked by dilute sulphuric or hydrochloric acid. The ordinary commercial metal is rapidly dissolved, yielding a solution of the sulphate or chloride with evolution of hydrogen. Nitric acid (suitably diluted with water) dissolves it to form the nitrate with evolution of nitrous oxide:—

$$4Zn + 10H(NO_3) = 4Zn(NO_3)_2 + 5H_2O + N_2O.$$

*Note.*—Zinc can also react with stronger nitric acid to form nitric oxide (compare copper).

The metal also reacts with solutions of sodium or potassium hydroxide, hydrogen being evolved and the zinc going into solution as the sodium or potassium derivative of zinc hydroxide:—

$$Zn + 2K(OH)aq = H_2 + Zn(OK)_2 aq.$$

*Note.*—Zinc hydroxide, although it usually behaves as a base, displays in this case the character of an acid. The compound $Zn(OK)_2$ is sometimes called 'potassium zincate.' [Compare the cases of tin, arsenic, and antimony above.]

## Reactions of Zinc Salts in Solution.

[Use a solution of zinc sulphate.]

(1) The solution, treated with an equal volume of **ammonium chloride** solution, then with **ammonia** solution (TILL ALKALINE) and then with **hydrogen sulphide** solution, gives a *white* precipitate of zinc sulphide, $ZnS$.

(2) **Sodium (or potassium) hydroxide** solution [add the reagent *gradually*] yields a *white* precipitate of zinc hydroxide, $Zn(OH)_2$, which is readily soluble in excess of the alkali to a clear solution (of the zincate, see above).

(3) The clear solution of sodium or potassium zincate prepared in No. (2) is divided into two parts.

(*a*) To one portion **ammonium chloride** solution is added. There is no precipitate formed, for zinc hydroxide is soluble in ammonium chloride solution as well as in alkalis.

(*b*) To the other portion **hydrogen sulphide** solution is added. A *white* precipitate of zinc sulphide is produced.

*Note.*—Compare these reactions with those given under aluminium, No. (3).

The reactions on charcoal (see Chapter VI) afford other characteristic tests for zinc.

## XVIII.

### ALUMINIUM.—Symbol **Al**; Atomic Weight, **27**.

### Trivalent.

**Formulae of chief compounds:**—

Oxide $Al_2O_3$ (*Alumina*) Hydroxide $Al(OH)_3$
Sulphate $Al_2(SO_4)_3$ Chloride $AlCl_3$
Nitrate $Al(NO_3)_3$.

**Properties of the metal.**—Aluminium is a white metal remarkable for its low specific gravity (2·6). It melts at a fairly high temperature, and is about as hard as silver.

**Action of air (or oxygen).**—Aluminium is not oxidized in air at ordinary temperatures. At a red heat aluminium burns, the finely divided metal giving a brilliant white flame, forming the oxide $Al_2O_3$. Aluminium at high temperatures has a remarkable affinity for oxygen and in combining with it gives rise to an extraordinary evolution of heat. A mixture of dry oxide of iron with aluminium powder is known as 'thermite' and is used for the rapid production of molten iron. When this mixture is ignited the reaction

$$3Fe_3O_4 + 8Al = 4Al_2O_3 + 9Fe.$$

proceeds with such vigour that both the alumina and the metallic iron are obtained in the molten state.

**Action on water.**—Pure water is not attacked by aluminium at ordinary temperatures, but in presence of certain salts (particularly sodium chloride), the metal is rapidly converted into the hydroxide when exposed to the air. At a red heat aluminium decomposes steam, forming the oxide with evolution of hydrogen.

**Action on acids.**—The metal dissolves readily in dilute sulphuric or hydrochloric acid, yielding a solution of the sulphate or chloride with evolution of hydrogen. Pure nitric acid, whether concentrated or dilute, scarcely attacks aluminium at all.

Aluminium also reacts with solutions of sodium or potassium hydroxide, hydrogen being evolved, and the metal going into solution as the sodium or potassium derivative of aluminium hydroxide:—

$$2Al + 6K(OH)aq. = 3H_2 + 2Al(OK)_3aq.$$

*Note.*—Aluminium hydroxide, although it usually behaves as a base, displays in this case the character of an acid. The compound $Al(OK)_3$ is called potassium aluminate. (Compare the case of zinc, p. 54.)

## Reactions of Aluminium Salts in Solution.

[Use a solution of aluminium sulphate or chloride.]

(1) The solution, treated with an equal volume of **ammonium chloride** solution, then with **ammonia** solution (TILL ALKALINE), and then with **hydrogen sulphide** solution, gives a *white* precipitate of aluminium *hydroxide*, $Al(OH)_3$.

*Note.*—Aluminium does not form any sulphide in the wet way. When the ammonia is added the white hydroxide of aluminium is precipitated and the addition of hydrogen sulphide does not affect it. (Compare the cases of ferrous and ferric salts and those of chromium.)

There is a sulphide of aluminium, formed by burning aluminium in sulphur vapour, but it is decomposed by water:—

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S.$$

(2) **Sodium (or potassium) hydroxide solution** [add the reagent *gradually*] yields a *white* precipitate of alu-

minium hydroxide, $Al(OH)_3$, which is readily soluble in excess of the alkali to a clear solution (of the aluminate, see above).

(3) The clear solution of sodium or potassium aluminate prepared in No. (2) is divided into two parts.

(*a*) To one portion **ammonium chloride** solution is added. A white precipitate of aluminium hydroxide is formed, for aluminium hydroxide is insoluble in ammonium chloride solution.

(*b*) To the other portion **hydrogen sulphide** solution is added. There is no precipitate formed, for, as explained above, aluminium sulphide does not exist in contact with water.

A further reaction, sometimes useful as a confirmatory test for aluminium salts, is the formation of Thénard's Blue on charcoal (see Chapter VI).

## XIX.

### CHROMIUM.—Symbol **Cr**; Atomic Weight, **52**.

In its *salts* chromium is **trivalent.**

This element forms several oxides. The common basic oxide is the green $Cr_2O_3$ (chromium sesquioxide). Of the other oxides only the trioxide $CrO_3$ is of any importance, and it is the anhydride of chromic acid $H_2(CrO_4)$ and bichromic acid $H_2(Cr_2O_7)$ from which are derived the chromates and the bichromates. These will be dealt with later under *acids*.

**Formulae of chief compounds:—**

Oxide $Cr_2O_3$ Hydroxide $Cr(OH)_3$
Sulphate $Cr_2(SO_4)_3$ Chloride $CrCl_3$
Nitrate $Cr(NO_3)_3$.

*Note.*—The chromium compounds are remarkable for the diversity of their colours. As a *metal* chromium yields salts which are either *green* or *violet* and most of the salts can exist in either a green or a violet form. As an acid-forming element it yields chromates and bichromates which are usually either yellow or red.

**Properties of the metal.**—Chromium is a very hard white metal which only melts at an exceedingly high temperature. In appearance it very much resembles iron.

**Action of air (or oxygen).**—The metal is not oxidized in air at ordinary temperatures. Even in oxygen it needs to be heated to a very high temperature (2000°) before it will burn. When it does so it forms the green oxide $Cr_2O_3$.

**Action on water.**—None.

**Action of Acids.**—This metal is not readily attacked by dilute acids, though both dilute sulphuric and dilute hydrochloric acid can dissolve it with evolution of hydrogen and formation, in the first instance, of unstable chromous salts (in which the metal is divalent): these however oxidize very rapidly in the air to the ordinary salts of trivalent chromium.

## Reactions of Chromium Salts in Solution.

[Use a solution of chromium sulphate or chloride].

(1) The solution, treated with an equal volume of **ammonium chloride** solution, then with **ammonia** solution (TILL ALKALINE) and then with **hydrogen sulphide** solution gives a *grey-green* precipitate of *chromium hydroxide*, $Cr(OH)_3$.

*Note.*—Here, as in the case of aluminium, there is no sulphide formed in the wet way. When the ammonia is added the greenish hydroxide of chromium is precipitated and the addition of hydrogen sulphide does not affect it.

(2) **Sodium (or potassium) hydroxide solution** [add the reagent *gradually*] yields a grey-green precipitate of chromium hydroxide, $Cr(OH)_3$, which is very readily soluble in excess of the alkali, forming a clear dark-green solution.

This solution is formed because the hydroxide of chromium, like those of zinc and of aluminium, can behave as an acid, yielding a 'chromite':—

$$Cr(OH)_3 + 3K(OH) = Cr(OK)_3 + 3H_2O.$$

(3) The clear solution (of sodium or potassium 'chromite') prepared in No. (2) is divided into two parts.

(*a*) One portion is well boiled. The precipitate of chromium hydroxide is re-formed.

This is because *boiling* water decomposes the soluble 'chromites':—

$$Cr(OK)_3 + 3H_2O = Cr(OH)_3 + 3KOH.$$

(*b*) To the other portion a little solid **sodium peroxide** is added and the mixture is warmed. The sodium peroxide acts as an oxidizing agent, the green colour of the 'chromite' disappears and in its place the **yellow** colour of the chromate is seen.

All the compounds of chromium impart to the borax bead a characteristic green colouration (see Chapter VI).

## XX.

## RECOGNITION OF ANY MEMBER OF GROUP III.

As already indicated (p. 44) the metallic radicals $Fe^{\cdot\cdot}$(ous), $Fe^{\cdot\cdot\cdot}$(ic), $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$ and $Cr^{\cdot\cdot\cdot}$ constitute a third **group** every member of which is characterized by the fact that its salts, in solution (while they do not yield precipitates either with dilute hydrochloric acid or with hydrogen sulphide in the presence of dilute hydrochloric acid), *give* **when treated with an equal volume of ammonium chloride solution, then ammonia solution (till alkaline) and then hydrogen sulphide solution** *a precipitate of the sulphide* (*or hydroxide*):—

$$[FeS, NiS, CoS, MnS, ZnS, Al(OH)_3 \text{ or } Cr(OH)_3].$$

**(a)** The precipitate yielded by ferrous, ferric, nickel or cobalt salts is **black.**

**(b)** That given by manganese salts is **pink.**

**(c)** Zinc salts and those of aluminium yield a **white** precipitate.

**(d)** The precipitate given by chromium salts is **grey-green.**

An inspection of the 'group-precipitate' will therefore enable an immediate classification into two main divisions to be made, viz :—

(i) a **black** group precipitate, $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Ni^{\cdot\cdot}$ or $Co^{\cdot\cdot}$,

(ii) a group precipitate that is **not black,** $Mn^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$ or $Cr^{\cdot\cdot\cdot}$.

In either case the reaction obtained when a **fresh portion of the original solution** is treated with **sodium (or potassium) hydroxide solution** will practically decide which of the various possible metallic radicals is actually present. The reaction of each of these metallic radicals with this reagent has already been examined, being in each case numbered (2) among the reactions described above.

(*a*) Salts of *zinc* and of *aluminium* give precisely similar results when treated with alkali (white precipitates, *soluble in excess of the reagent*), but they can be distinguished from one another by applying to this solution of the precipitate in excess of alkali the tests described under (3) in the reactions of the salts of these metals.

(*b*) But all the others ($Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$) give distinct and unmistakeably different reactions with *sodium or potassium hydroxide.*

> *Note.*—**The student is advised to tabulate the reactions of these metallic radicals with sodium (or potassium) hydroxide so as to have them readily available for reference.**

Of course in each case further *confirmatory* tests must be applied.

(*c*) **It sometimes happens that the Group III reagents** ($NH_4Cl$ aq. + $NH_3$ aq. + $H_2S$ aq.) **produce a precipitate which is not black (almost always a white one).** This would of course suggest the presence of zinc or of aluminium, but on proceeding to test a fresh portion of the original solution with sodium or potassium hydroxide solution, a *white* (or at all events *light-coloured*) *precipitate* is obtained **which is not soluble in excess of the alkali** (absence of $Zn^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$ and $Cr^{\cdot\cdot\cdot}$) **and does not darken when shaken with air** (absence of $Mn^{\cdot\cdot}$).

In such a case we are assured of the absence of all the metals of Group III, and it follows that the metallic radical of the salt under examination must be one of those not yet discussed.

Now these are *barium*, *strontium*, *calcium*, *magnesium*, *ammonium*, *potassium* and *sodium*.

**A salt which behaves in this way is always found to be insoluble in water but soluble in dilute hydrochloric acid.**

But all the salts of ammonium, potassium and sodium are soluble in water. Therefore such a salt as we are discussing *must have either barium, or strontium, or calcium, or magnesium, for its metallic radical.*

The question arises, why are these metals precipitated here, in Group III, to which they do not really belong?

The answer is that they are not 'precipitated' at all in the sense in which those truly belonging to the group are precipitated. There are certain salts of barium, strontium, calcium, and magnesium (particularly the phosphates, oxalates, borates, or fluorides) which are insoluble in water and require the presence of dilute acids (e.g. HCl aq.) to keep them dissolved.

When this acid is *neutralized* [as it is by the ammonia in the Group-test or by the alkali in test No. (2)] the **salt itself** is simply deposited, and so gives the appearance of a precipitate.

It is therefore necessary, when this particular case arises, to test for barium, strontium, calcium or magnesium by reactions which can be applied without neutralizing the acid required to keep the salt in solution.

An account of these is given at the end of the sections dealing with the remaining metallic radicals.

## XXI.

## METALS OF GROUP IV.

The metallic radicals which are not precipitated either by dilute hydrochloric acid (Group I), or by hydrogen sulphide in the presence of dilute hydrochloric acid (Group II), or by 'ammonium sulphide' in presence of ammonium chloride (Group III), are **barium, strontium, calcium, magnesium, ammonium, potassium** and **sodium.**

Of these seven, the three first named are distinguished from the rest by the fact that their **carbonates** are insoluble in ammonium chloride solution, and so are precipitated on adding **ammonium carbonate** solution to a solution of the salt which already contains **ammonium chloride and free ammonia.**

These three metals, barium, strontium and calcium, thus constitute a fourth '**group,**' the members of which we have now to examine.

## BARIUM.—Symbol **Ba**; Atomic Weight, **137·5.**

**Divalent.**

**Formulae of chief compounds** :—

Oxide $BaO$ Hydroxide $Ba(OH)_2$
Chloride $BaCl_2$ Nitrate $Ba(NO_3)_2$
Sulphate $Ba(SO_4)$ Carbonate $Ba(CO_3)$.

In addition to the ordinary basic oxide $BaO$ (baryta) which is a grey solid that unites eagerly with water to form the hydroxide $Ba(OH)_2$ [compare the slaking of quicklime] there is also another oxide of barium, of formula $BaO_2$, which is called barium dioxide or peroxide. It is produced when the monoxide (baryta) is heated in a current of air or oxygen to a temperature just short of a red heat. This dioxide, when it is acted upon by dilute acids, yields the barium salt of the acid employed and hydrogen peroxide, $H_2O_2$ :—

$$BaO_2 + 2HCl \text{ aq.} = BaCl_2 \text{ aq.} + H_2O_2 \text{ aq.}$$

When heated alone, especially under reduced pressure, it evolves oxygen, leaving a residue of baryta.

**Properties of the metal.**—The metal itself is very little known. It is described as a white metal, resembling tin in appearance, and being about as soft as lead. It melts and volatilizes only at very high temperatures.

**Action of air (or oxygen).**—The metal oxidizes rapidly in the air, forming the oxide $BaO$, evolving heat, and finally becoming red-hot.

**Action on water.**—The metal acts readily upon cold water, barium hydroxide, $Ba(OH)_2$, being formed and hydrogen liberated.

It is unnecessary to consider the action of acids upon a metal which thus decomposes cold water, since each acid would simply react with the barium hydroxide formed.

## Reactions of Barium Salts in Solution.

[Use a solution of barium chloride or nitrate].

(1) The solution, treated with an equal volume of **ammonium chloride** solution, then with **ammonia** solution (*till alkaline*) and then with **ammonium carbonate** solution, gives a *white* precipitate of barium carbonate, $Ba(CO_3)$.

If this precipitate of barium carbonate be allowed to settle (which it will do far better if the liquid be first boiled), the supernatant liquid poured off, and the $Ba(CO_3)$ dissolved in the least possible amount of *acetic acid*, a solution of barium acetate, $Ba(C_2H_3O_2)_2$, is formed, which can be used for the next test.

(2) If a *small quantity* of *boiling* **potassium chromate** solution be added drop by drop to the *boiling* solution of barium acetate (prepared as above) a *lemon-yellow* precipitate of barium chromate, $Ba(CrO_4)$, is formed.

*Note.*—This reaction is extremely characteristic. It is given neither by strontium nor by calcium salts and so serves to distinguish barium from the other two members of this group. Since however barium chromate is dissolved by hydrochloric acid (and other mineral acids) it is safest thus to carry it out with the *acetate* solution. The object of boiling the solutions is to obtain a granular precipitate that settles well.

(3) **Calcium sulphate solution** produces, even in the presence of acids, an IMMEDIATE *white* precipitate of barium sulphate, $Ba(SO_4)$.

The green colouration imparted to the Bunsen flame by barium chloride (see Chapter VI) is very characteristic.

## XXII.

### STRONTIUM.—Symbol **Sr**; Atomic Weight, **87·5.**

**Divalent.**

**Formulae of chief compounds**:—

Oxide SrO
Chloride $SrCl_2$
Sulphate $Sr(SO_4)$
Hydroxide $Sr(OH)_2$
Nitrate $Sr(NO_3)_2$
Carbonate $Sr(CO_3)$.

**Properties of the metal.**—Strontium is white and closely resembles barium, but melts at a higher temperature.

**The action of air (or oxygen)** and the **action on water** resemble those of barium, but are somewhat less energetic.

### Reactions of Strontium Salts in Solution.

[Use a solution of strontium chloride].

(1) The solution, treated with an equal volume of **ammonium chloride** solution, then with **ammonia** solution (*till alkaline*), and then with **ammonium carbonate** solution, gives a *white* precipitate of strontium carbonate, $Sr(CO_3)$.

(2) A **cold** dilute solution of a strontium salt, treated with dil. HC ~~**ammonia** (*till alkaline*)~~ and then with **ammonium sulphate**, $(NH_4)_2(SO_4)$, solution, gives a *white* precipitate of strontium sulphate, $Sr(SO_4)$, which comes down gradually.

(3) **Calcium sulphate solution** produces *no immediate precipitate* (contrast barium) but after standing a short time, and more particularly if the solution be warmed, a *white* precipitate of strontium sulphate, $Sr(SO_4)$, is *gradually* formed.

*Note.*—It will depend very much upon the strength of the strontium salt solution used how long this precipitate takes to make its appearance. If the solution be strong the precipitate appears very quickly, but if dilute, may take several minutes.

The test is valuable because, like the corresponding test for barium (No. 3) it is applicable even in the presence of dilute acids (HCl aq or $H(NO_3)$aq).

The crimson colouration imparted to the Bunsen flame by strontium chloride (see Chapter VI) is very characteristic.

# XXIII.

## CALCIUM.—Symbol **Ca**; Atomic Weight, **40**.

**Divalent.**

**Formulae of chief compounds:—**

| | |
|---|---|
| Oxide CaO (quicklime) | Hydroxide $Ca(OH)_2$ (slaked lime) |
| Chloride $CaCl_2$ | Nitrate $Ca(NO_3)_2$ |
| Sulphate $Ca(SO_4)$ | Carbonate $Ca(CO_3)$ |

Oxalate $Ca(C_2O_4)$.

**Properties of the metal.**—Calcium is a white metal, considerably harder than lead, which melts at a red heat (more easily than barium).

**Action of air (or oxygen).**—Calcium is fairly stable in air or oxygen as long as it is dry. When heated (to about 300°) it takes fire and burns, with a brilliant white light, to form the oxide, CaO.

**Action on water.**—The metal decomposes cold water, with evolution of hydrogen and formation of slaked lime, $Ca(OH)_2$. The action is less energetic than that of barium and strontium.

### Reactions of Calcium Salts in Solution.

[Use a solution of calcium chloride.]

(1) The solution, treated with an equal volume of **ammonium chloride** solution, then with **ammonia** solution (TILL ALKALINE) and then with **ammonium carbonate** solution, gives a *white* precipitate of calcium carbonate, $Ca(CO_3)$.

If this precipitate of calcium carbonate be allowed to settle (which it will do far better if the liquid be first boiled), the supernatant liquid poured off and the $Ca(CO_3)$ dissolved in the least possible amount of *acetic acid*, a solution of calcium acetate, $Ca(C_2H_3O_2)_2$, is formed which can be used for the next test.

(2) If a *boiling* solution of **ammonium oxalate** be added

to the *boiling* solution of calcium acetate (prepared as above) a *white* precipitate of calcium oxalate, $Ca(C_2O_4)$ is formed.

> *Note.*—This is a very useful reaction and since it is prevented by mineral acids (such as HCl aq.) it is safest always to carry it out with the *acetate* solution. The object of *boiling* both solutions is that the precipitate may be granular and settle well.

(3) **Dilute sulphuric acid** added to a solution of a calcium salt, mixed with an equal volume of *dilute hydrochloric acid*, does **not** produce any precipitate, but, if **alcohol** be now added, a *white* precipitate of calcium sulphate, $Ca(SO_4)$, will separate.

> *Note.*—Care must be taken to use either absolute alcohol or else purified methylated spirit which does not produce a turbidity with water.

The orange-red colour imparted to a Bunsen flame by calcium chloride (see Chapter VI) is very characteristic.

## XXIV.

## RECOGNITION OF ANY MEMBER OF GROUP IV.

The characteristic reaction of the metallic radicals $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ca^{\cdot\cdot}$ is the formation of the white precipitate of carbonate by addition of **ammonium carbonate solution in presence of ammonium chloride and ammonia.**

But a white precipitate so obtained may be either $Ba(CO_3)$, $Sr(CO_3)$ or $Ca(CO_3)$.

To distinguish between these, *boil the solution containing the precipitate and allow the latter to settle.* Then pour off the supernatant liquid as completely as possible and *dissolve the precipitate in the smallest quantity of acetic acid which will serve to give a clear solution.*

Divide this solution into three parts and examine these separately as follows:—

(**a**) Test the *first* portion for **barium** (by means of potassium chromate—see Reaction No. 2 of Barium).

If the lemon-yellow precipitate of $Ba(CrO_4)$ be formed apply a confirmatory test [$Ca(SO_4)$ aq.—Reaction No. 3 of Barium] to another of the portions.

(**b**) But should no barium chromate be formed, *infer the absence of barium*, take the *second* portion, and test it for **strontium** (by adding ammonia till it is alkaline and then ammonium sulphate—see Reaction No. 2 of Strontium).

If the characteristic gradual precipitation of $Sr(SO_4)$ be observed, apply to the remaining portion a confirmatory test [$Ca(SO_4)$ aq.—see Reaction No. 3 of Strontium].

(**c**) But should no precipitate of strontium sulphate be formed, take the *third* portion and test it for **calcium** (by means of ammonium oxalate—see Reaction No. 2 of Calcium). Confirm the presence of calcium by the reaction with dilute sulphuric acid and alcohol (see Reaction No. 3 of Calcium).

(**d**) Finally, confirm the conclusion at which you have arrived by performing the **flame test** for barium, strontium or calcium (as described in Chapter VI).

## *ADDENDUM.*

Recognition of *barium*, *strontium* or *calcium* in those cases *where they are precipitated in Group III.*

It was mentioned (on p. 60) that certain salts of barium, strontium and calcium (as well as of magnesium), which are insoluble in water but soluble in dilute acids, are deposited unchanged, by the addition of ammonia, in carrying out the test for Group III.

It was also explained how, **by the reaction with sodium (or potassium) hydroxide** the cases where this has occurred can easily be distinguished from true 'precipitations' given by members of Group III.

In these cases it is impossible to apply any of the tests given above for $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$ or $Ca^{\cdot\cdot}$ in which the solution has to be rendered alkaline by the addition of ammonia. It is thus impossible to obtain the precipitates of the carbonates of which we have made use, and we are driven to rely only upon those tests which can be carried out in dilute hydrochloric acid solution.

The procedure will, then, be as follows:—

(i) To a portion of the original solution (in dilute HCl aq.) an excess of **calcium sulphate** solution is added.

(*a*) An **immediate** *white* precipitate indicates the presence of Ba¨ (see Reaction No. 3 of Barium).

(*b*) A *white* precipitate forming **only after some time** indicates the presence of Sr¨ (see Reaction No. 3 of Strontium).

(*c*) If there be *no precipitate, even after the lapse of several minutes*, infer the absence of barium and strontium. The original solution must now contain either a calcium or a magnesium salt.

(ii) Test a fresh portion of the original solution for calcium by means of **dilute sulphuric acid and alcohol** (see Reaction No. 3 of Calcium).

(*a*) *A white* precipitate indicates the presence of Ca¨.

(*b*) If there be *no precipitate* the absence of calcium is assured and the solution contains a magnesium salt. (For the procedure to be adopted with this see *Magnesium* below).

If either Ba¨, Sr¨ or Ca¨ have been detected by the above reactions its presence must be confirmed by applying the **flame test which, in these particular cases, must be carried out as follows**:—

A portion of the original solid salt (finely powdered) is boiled for some considerable time with **sodium carbonate** solution. By this means *some* of the salt is converted into the carbonate, e.g.

$$Ca_3(PO_4)_2 + 3Na_2(CO_3)\text{ aq.} = 3Ca(CO_3) + 2Na_3(PO_4)\text{ aq.}$$

After being well boiled, the mixture is filtered and the residue upon the paper, **having been thoroughly washed, several times, with hot water,** is treated with a few drops of dilute hydrochloric acid. This forms a solution of the chloride, dissolving the carbonate, and this chloride solution is caught upon a watch-glass and used for the flame test (see Chapter VI).

## XXV.

### METALS OF 'GROUP V.'

The remaining common metallic radicals include the metals magnesium, potassium and sodium and the compound-radical ammonium ($NH_4$). These are classed together, not because they possess one reaction common to them all, like the members of the preceding groups, but because they are not precipitated by any of the reagents so far applied.

They must be tested for **one by one** in the order:—

(i) magnesium,
(ii) ammonium,
(iii) potassium,
(iv) sodium ,

by means of the reactions given below.

### MAGNESIUM.—Symbol **Mg**; Atomic Weight, **24·5**.

**Divalent.**

**Formulae of chief compounds**:—

Oxide $MgO$
Chloride $MgCl_2$
Sulphate $Mg(SO_4)$
Hydroxide $Mg(OH)_2$
Nitrate $Mg(NO_3)_2$
Carbonate $Mg(CO_3)$.

**Properties of the metal.**—Magnesium is a white metal of extremely low density (1.75 grms. per cc.). It is malleable and ductile, and is fairly hard. It does not melt below a red heat, but is volatile at high temperatures, and can be distilled.

**Action of air (or oxygen).**—The metal is stable in dry air at ordinary temperatures, but when heated takes fire, below its melting point, and burns with a bright light, to magnesium oxide, $MgO$

**Action on water.**—Magnesium does not attack cold water. Boiling water is *slowly* decomposed, hydrogen being evolved and magnesium hydroxide formed. Heated magnesium burns brilliantly in steam, forming MgO and liberating hydrogen.

## Reactions of Magnesium Salts in Solution.

[Use a solution of magnesium sulphate or chloride.]

(1) The solution, treated with an equal volume of **ammonium chloride** solution, then with **ammonia** solution (TILL ALKALINE) and then with **sodium (or ammonium) phosphate** solution, gives a *white* precipitate of magnesium ammonium phosphate, $Mg(NH_4)(PO_4)$.

*Note.*—Either sodium phosphate, $Na_2H(PO_4)$, or ammonium phosphate, $(NH_4)_3(PO_4)$, will serve for this reaction, but a solution of microcosmic salt, $Na(NH_4)HPO_4$, will be found to act better than either.

(2) **Sodium carbonate** solution gives a *white* precipitate of magnesium carbonate, $Mg(CO_3)$, *which is easily soluble in ammonium chloride solution.*

*Note.*—The solubility of both the hydroxide and the carbonate of magnesium in ammonium chloride solution serves to prevent the precipitation of this metal in Groups III and IV and is one of the chief reasons for the addition of ammonium chloride in testing for those groups.

Magnesium salts, when heated strongly on charcoal in the blowpipe flame, yield the oxide, and this, if moistened with cobalt nitrate solution and re-heated, acquires a faint pink colour (compare the corresponding reactions of zinc and of aluminium salts described in Chapter VI). The test, however, is not very satisfactory.

## *ADDENDUM.*

Recognition of *magnesium* in those cases *where it is precipitated in Group III.*

When the reagents for Group III have produced a white precipitate, and when **sodium (or potassium) hydroxide** solution has given a **white precipitate insoluble in excess and not darkening when shaken with air,** the metallic radical present is necessarily either $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ca^{\cdot\cdot}$ or $Mg^{\cdot\cdot}$.

It has been shown, in the Addendum to Group IV, how the presence of $Ba^{\cdot\cdot}$ or $Sr^{\cdot\cdot}$ or $Ca^{\cdot\cdot}$ can be recognized. If the tests there given show that neither $Ba^{\cdot\cdot}$ nor $Sr^{\cdot\cdot}$ nor $Ca^{\cdot\cdot}$ is present it becomes necessary to find some means of testing for magnesium in such a case.

A portion of the original solid salt (finely powdered) is **boiled** for several minutes with **sodium carbonate** solution. The mixture is filtered. The *residue* upon the filter-paper will now contain some *magnesium carbonate.* Now magnesium carbonate is soluble in ammonium chloride solution and can therefore be *dissolved* by pouring a few ccs. of *ammonium chloride solution* into the filter. The clear solution is caught in a clean test-tube and treated with *ammonia* (till alkaline) and then *sodium* (*or ammonium*) *phosphate.* The white precipitate of $Mg(NH_4)(PO_4)$ will prove the presence of magnesium.

## XXVI.

### AMMONIUM.—Symbol $(\mathbf{NH_4})$; Combining Weight, **18.**

### Monovalent.

Ammonia gas, $NH_3$, when it neutralizes acids, combines with the whole of the acid [e.g. $NH_3 + HCl = (NH_4)Cl$], and the resulting salts possess the formulae and properties which would be expected to belong to salts formed by the reaction of a base $(NH_4)(OH)$ with the acids in question. Hence it is customary to consider the group of atoms $(NH_4)^{\cdot}$ as constituting a 'metallic radical' analogous to $K^{\cdot}$ or $Na^{\cdot}$. This radical has received the name 'ammonium.'

All attempts to prepare ammonium itself, in the free state, have so far failed.

The solution of ammonia in water is often called 'ammonium hydrate,' but the compound $(NH_4)(OH)$ cannot be isolated, and in this book we have, throughout, spoken of this solution simply as 'ammonia solution.'

**Formulae of chief compounds** :—

| | |
|---|---|
| Chloride $(NH_4)Cl$ | Nitrate $(NH_4)(NO_3)$ |
| Sulphate $(NH_4)_2(SO_4)$ | Carbonate $(NH_4)_2(CO_3)$. |

### Characteristic Reaction of Ammonium Compounds.

If any ammonium salt be ground with powdered lime (CaO) in a mortar, and enough water be added to make a thick paste, **ammonia gas** is evolved which can be recognized by

(i) its smell;

(ii) its action on moistened red litmus paper (turns blue);

(iii) its action on moistened turmeric paper (turns brown).

*Note.*—The test papers should be held well above the upper edge of the mortar. They must on no account come in contact with the lime, since this of course has itself an alkaline reaction.

### Reactions of Ammonium Salts in Solution.

[Use a solution of ammonium chloride].

(1) **Chloroplatinic acid,** $H_2(PtCl_6)$, solution gives a *crystalline yellow* precipitate of ammonium chloroplatinate $(NH_4)_2(PtCl_6)$. ?

*Note.*—This reagent is often wrongly called 'platinum tetrachloride.' It is the product formed when platinum is dissolved in aqua regia. Owing to the high price of platinum the reagent is very costly and should be used sparingly.

It is best to carry out the test upon a small watch glass. The precipitate appears more readily if the glass is rubbed with the rounded end of a glass rod, the crystals forming along the lines of the rubbing.

(2) **Sodium hydrogen tartrate,** $NaH(C_4H_4O_6)$, solution *in the presence of sodium acetate solution, and enough acetic acid to render the solution distinctly acid* (*if it be not so already*), gives a white crystalline precipitate of ammonium hydrogen tartrate $(NH_4)H(C_4H_4O_6)$.

*Note.*—This test also is best carried out upon a watch glass. The ammonium salt solution must not be too dilute, and the precipitate appears much more readily if the glass is rubbed as above.

~~(3) **Sodium picrate** solution, *in presence of sodium carbonate solution*, gives, on shaking, a *yellow, highly crystalline precipitate* of ammonium picrate.~~

Any one of these three tests will serve as a *confirmatory* test for ammonium, but it must be remembered that they are only valid for this purpose *after* the characteristic reaction with lime has been observed, for all these three reactions are *also* given by *potassium* salts.

## POTASSIUM.—Symbol **K** (*Kalium*); Atomic Weight **39.**

### Monovalent.

**Formulae of chief compounds:—**

[Oxide $K_2O$]
Chloride $KCl$
Sulphates $K_2(SO_4)$
and $KH(SO_4)$

Hydroxide $K(OH)$
Nitrate $K(NO_3)$
Carbonates $K_2(CO_3)$
and $KH(CO_3)$

**Properties of the metal.**—Potassium is a white metal which melts very easily (about 66°C) and is so soft that it can be cut with a knife.

**Action of air (or oxygen).**—A freshly cut surface tarnishes almost instantly in the air, and a piece of the metal exposed to the air very rapidly oxidizes, growing hot. The product, in moist air, is chiefly the hydroxide $K(OH)$, which is rapidly converted into carbonate by atmospheric carbon dioxide. Both the hydroxide and the carbonate are deliquescent, and the final product of the action of air on potassium is a semi-liquid mass [$K(OH) + K_2(CO_3)$aq.]. Heated potassium burns in air to a peroxide $K_2O_4$.

**Action on water.**—Potassium acts violently upon water, liberating hydrogen and forming the hydroxide $K(OH)$. This reaction is attended with the evolution of much heat, so that the hydrogen evolved takes fire and burns, the flame being coloured lilac by the vapour of potassium.

Of course, **acids** would act with dangerous violence upon metallic potassium, and its salts are always made, not from the metal, but from the carbonate or hydroxide.

## Reactions of Potassium Salts in Solution

[Use a solution of potassium nitrate].

*Recall, what was said on p. 73, that the salts of ammonium give precisely similar reactions in solution to those of potassium.*

**It is necessary to be sure of the absence of ammonium salts before attempting to apply tests for potassium salts in solution.**

(1) **Chloroplatinic acid,** $H_2(PtCl_6)$, solution gives a *crystalline yellow* precipitate of potassium chloroplatinate $K_2(PtCl_6)$.

*Note.*—This reaction should be carried out in the same way as the corresponding reaction given under ammonium salts.

(2) **Sodium hydrogen tartrate,** $NaH(C_4H_4O_6)$, solution, *in the presence of sodium acetate solution and enough acetic acid to render the solution distinctly acid* (*if it be not so already*), gives a white crystalline precipitate of potassium hydrogen tartrate $KH(C_4H_4O_6)$.

*Notes.*—(i) This reaction should be carried out upon a watch glass and the surface of the glass should be rubbed as in the case of the corresponding test for ammonium.

(ii) One of the commonest potassium salts is this very $KH(C_4H_4O_6)$, 'cream of tartar,' and it is obvious that this test will not apply to that salt. One or more of the others here given must be used in that case.

(3) **Sodium picrate solution,** *in presence of enough sodium carbonate solution to render the solution alkaline,* gives, **on shaking** a *feathery yellow* precipitate of potassium picrate.

The *lilac* colouration imparted to a Bunsen flame by potassium salts (see Chapter VI) is very characteristic.

## SODIUM.—Symbol **Na** (*Natrium*); Atomic Weight, **23.**

**Monovalent.**

**Formulae of chief compounds**:—

| | |
|---|---|
| [Oxide $Na_2O$] | Hydroxide $Na(OH)$. |
| Chloride $NaCl$ | Nitrate $Na(NO_3)$ |

Sulphates $Na_2(SO_4)$ and $NaH(SO_4)$
Carbonates $Na_2(CO_3)$ and $NaH(CO_3)$.

In addition to the oxide $Na_2O$, which is only known as the product of the action of metallic sodium upon sodium hydroxide, and whose very existence is doubtful, there is a sodium peroxide, $Na_2O_2$, which is formed by burning the metal in air or in oxygen. This is analogous to the barium peroxide already described, inasmuch as, with dilute acids, it yields the salts corresponding to the oxide $Na_2O$, together with hydrogen peroxide.

**Properties of the metal.**—Sodium is, like potassium, a white metal of low melting point (96°C) which is soft enough to be cut with a knife.

**Action of air (or oxygen).**—A freshly-cut surface tarnishes quickly, but not so fast as one of potassium. If left exposed to air, sodium finally gives a dry residue of sodium carbonate (compare potassium). Heated sodium burns brightly in air to form sodium peroxide, $Na_2O_2$.

**Action on water.**—The action is similar to, but less violent than, that of potassium. The hydrogen evolved does not take fire of itself.

### Reaction of Sodium Salts in Solution.

[Use a solution of sodium chloride].

A freshly prepared solution of **potassium antimonate,** $K(SbO_3)$, gives, when *boiled* with a solution of a sodium salt *made alkaline with* **potassium hydroxide** solution, a *heavy granular white* precipitate of sodium antimonate.

*Note.*—The solution of potassium antimonate is prepared by dissolving a small pinch of the solid salt in a cc. or so of *boiling* water. This solution is *filtered into* the sodium salt solution (to which K(OH)aq. has already been added) and the whole is boiled. The sodium antimonate settles at once as a very dense powder. Its composition is $2Na(SbO_3) + H_2O$ or $Na_2H_2(Sb_2O_7)$.

The only other characteristic reaction possessed by sodium salts is the intense and persistent *yellow* colouration imparted by them to a Bunsen flame (see Chapter VI).

*Note.*—The light from this sodium flame has one very characteristic quality, namely that it is entirely absorbed by vermilion (mercuric sulphide) and as completely reflected by mercuric iodide. Both salts are, in ordinary light, scarlet. By 'sodium light' the vermilion appears nearly black (dark grey) while the mercuric iodide appears white. It is enough to make smears of each side by side upon a piece of white paper or card and fold this so that it can be held 'round' the flame.

**N.B.—Before attempting to analyse an unknown substance, make a careful study of CHAPTER V.**

# CHAPTER III.

## Classification of the Common Acid Radicals.

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### XXVII.

There are two general methods of classifying and detecting the acid radicals of simple salts. One of these serves to arrange them in **three** main **divisions** and depends upon the action of (*a*) dilute hydrochloric acid and (*b*) strong sulphuric acid on the solid salt. The other admits of their division into **six** definite **groups** and depends upon the reactions of the salts in solution with (*a*) silver nitrate and (*b*) barium chloride solutions.

The latter of these methods is certainly the more precise and effective, but it can be applied only when a suitable *solution* has been obtained, and it is not always easy to prepare such a solution. So that the former plan frequently affords a shorter and easier method of detection. We shall therefore make a study of both methods and use the one or the other as may be most convenient in any particular case.

1. *Division of acid radicals according to the reactions of their salts with* (*a*) *dilute hydrochloric and* (*b*) *concentrated sulphuric acid.*

**(A)**—Acid radicals whose salts are acted upon by **dilute hydrochloric acid** include *all*

**carbonates, nitrites, hypochlorites, sulphites, thiosulphates, chlorates, acetates,** and *some* **sulphides** and **cyanides.**

**(B)**—Acid radicals whose salts are *not* attacked by dilute hydrochloric acid but react with **concentrated sulphuric acid** include *all*

**fluorides, oxalates, [cyanides], [formates, ferrocyanides, ferricyanides, sulphocyanides, tartrates, nitrates, [chlorates], permanganates,** and *nearly all* **chlorides, bromides,** and **iodides.**

**(C)**—Acid radicals whose salts give no definite recognizable reaction with either dilute hydrochloric or concentrated sulphuric acid include *all*

**phosphates, sulphates, borates, [arsenates,] chromates,** and **iodates.**

Details of the reactions given by each member of the divisions **A** and **B** are supplied under the individual acids, below, but before it is attempted to verify them the method of carrying out these tests must be noted carefully and followed exactly in every case.

**To examine the action of an acid upon a solid salt:**—Take a SMALL and DRY test-tube, place in it about a gramme of the FINELY POWDERED salt. Pour upon this enough of the acid to cover the powder to a depth of one or two centimetres. Take care that the powder is thoroughly mixed with the acid. Observe (and record) what happens while cold, and, failing a reaction then, heat the contents of the tube gradually but DO NOT BOIL. Observe (and record) any reaction which occurs when hot.

*Notes.*—(i) Most of the characteristic reactions involve the evolution of a gas, the escape of which is, in most cases, accompanied by *effervescence*, but effervescence must not be confused with mere boiling. Effervescence will continue after the source of heat has been withdrawn.

(ii) When it is desired to examine the action of a gas upon a particular reagent, the tube in which the gas is being evolved should be closed with the thumb till a distinct pressure is felt. The reagent is placed in another test-tube and, by slightly raising the end of the thumb, the compressed gas is allowed to shoot into the reagent-tube which is held aslant. This, in turn, is covered with the other thumb and shaken up.

(iii) It very frequently happens that, on warming a salt with concentrated sulphuric acid, sulphur dioxide is evolved. Now the only salts commonly met with, from which acids liberate sulphur dioxide are sulphites and thiosulphates, and from these it is liberated by dilute hydrochloric acid, so that they should have been recognised at once and there is no excuse for treating them with strong sulphuric acid at all. In any other case the sulphur dioxide must come *from the decomposition of the sulphuric acid itself.* This always means that the hot strong sulphuric acid is behaving as an oxidizing agent, $H_2(SO_4) = H_2O + SO_2 + [O]$, the oxygen being taken by the substance introduced. Now so many substances are oxidizable that this evolution of $SO_2$ may mean very many things, and cannot be taken as a simple indication of the presence of any one substance.

A very frequent case, and one which it is important to bear in mind, is that of insoluble sulphides (not acted on by dilute hydrochloric acid and so not detected in the first systematic test). These react as follows :—

$$MS + H_2(SO_4) = M(SO_4) + H_2S$$
$$H_2S + 3H_2SO_4 = 4H_2O + 4SO_2.$$

Hence when the evolution of $SO_2$ is very marked, it is always well to enquire whether the salt is an insoluble sulphide.

**2.** *Division of the acid radicals into* **Groups** *by comparing the reactions of their salts, in solution, with solutions of* (a) *silver nitrate and* (b) *barium chloride.*

*Note.*—In case the metallic radical of a salt should have been found to be *silver*, *mercury(-ous)* or *lead*, it is necessary to use barium **nitrate** solution because the chloride would, in any case, give a white precipitate (of AgCl, $Hg_2Cl_2$ or $PbCl_2$). It must therefore be borne in mind that, where *barium chloride* is specified as a reagent, the *nitrate* is to be substituted when the metallic radical is $Ag^{\cdot}$, $Hg_2^{\cdot\cdot}$, or $Pb^{\cdot\cdot}$.

[*The names of salts of less common occurrence are enclosed in brackets.*]

**Group I.**—Acid radicals whose salts yield, in solution, a **precipitate with silver nitrate solution which is insoluble in cold dilute nitric acid,** and **no precipitate with barium chloride solution :—**

**chlorides, bromides, iodides, cyanides, [ferrocyanides], [ferricyanides], [sulphocyanides], sulphides, [hypochlorites].**

**Group II.**—Acid radicals whose salts, in solution, yield a **precipitate with silver nitrate solution** which is **soluble in cold dilute nitric acid** and **no precipitate with barium chloride solution :—**

**nitrites, acetates, [formates], [cyanates].**

**Group III.**—Acid radicals whose salts yield, in solution, a **white precipitate with silver nitrate solution** and a **white precipitate with barium chloride solution,** *both of which precipitates are soluble in cold dilute nitric acid,*

**carbonates, sulphites, oxalates, tartrates, borates, [iodates], [pyrophosphates], [metaphosphates].**

**Group IV.**—Acid radicals whose salts yield, in solution, a **coloured precipitate with silver nitrate solution** and a **precipitate with barium chloride solution,** *both of which precipitates are soluble in cold dilute nitric acid,*

**phosphates** (orthophosphates), **chromates, [thiosulphates], arsenates, [arsenites].**

**Group V.**—Acid radicals whose salts yield, in solution, **no precipitate with silver nitrate solution** but a **white precipitate with barium chloride solution** which is *insoluble in cold dilute nitric acid* :—

**sulphates, fluorides, [fluosilicates].**

**Group VI.**—Acid radicals whose salts yield, in solution, **no precipitate with either silver nitrate or barium chloride solutions** :—

**nitrates, chlorates, [perchlorates], [permanganates].**

In cases where a salt is soluble in water, it is always desirable to discover to which of these six groups the acid radical of it should be assigned, since, in this way, the field of investigation is at once restricted, usually within narrow limits. As often as not the colour, or other characteristics, of the precipitate obtained (particularly with silver nitrate) will afford so much information that tests for some one particular acid radical may properly, and successfully, be applied at once.

But it must not be forgotten that these reactions with silver nitrate and barium chloride (or nitrate) require, in most cases, that the aqueous solution should be neutral or at all events **not acid.**

Acid salts are occasionally encountered whose solutions in water are strongly acid. For example, the acid oxalate of potassium, $KH(C_2O_4)$, when dissolved in water, acts practically like a mixture of potassium oxalate with oxalic acid, and will not give the normal reactions described below as those of a soluble neutral oxalate. In the cases of salts which thus give strongly acid solutions (acid enough not only to redden blue litmus but also to dissolve sodium carbonate with effervescence) it is necessary, before attempting to discover their reactions with silver nitrate and barium chloride, to *neutralize* them with *dilute* ammonia solution.

With salts that are insoluble in water it is, very often, wholly unnecessary to prepare a neutral solution for these tests. In any case they should first be examined carefully by means of dilute hydrochloric acid (see above), and, if that does not give any characteristic reaction, afterwards with concentrated sulphuric acid. When both these tests fail the acid radical must be one of the few mentioned on p. 78 above and special tests should be applied for them in turn, as given in Chapter V below.

In that Chapter will also be found a brief account of the way in which a neutral solution, suitable for silver nitrate and barium chloride testing, can often be prepared from a salt insoluble in water.

NOTE.—**The student is advised, in verifying the reactions described below, to tabulate for himself the behaviour of the various acid radicals with (a) silver nitrate and (b) barium chloride solutions, and to arrange them in Groups, as above.**

## ACIDS OF GROUP I.

### XXVIII.

### Hydrochloric Acid and Chlorides.

Formula of acid, **HCl.** **Monobasic.**

The compound HCl, hydrogen chloride, is a gas, extremely soluble in water. It is to this solution in water that the name 'hydrochloric acid' is applied.

**Examples of Salts :—**

| | |
|---|---|
| Sodium chloride | $NaCl$ |
| Calcium chloride | $CaCl_2$ |
| Aluminium chloride | $AlCl_3$. |

**Solubility of salts.**—The *chlorides*, except $AgCl$, $Hg_2Cl_2$ and $PbCl_2$, are *soluble in water*, and of these three $PbCl_2$ will dissolve easily in *boiling* water, but crystallizes out on cooling.

*Note.*—The basic chlorides of bismuth and antimony $(BiO)Cl$ and $(SbO)Cl$ (see pp. 29 and 39) are insoluble in water but soluble in dilute acids. Mercurous chloride is dissolved by aqua regia (being oxidized to mercuric chloride).

### Reactions of Chlorides.

[Use dry sodium chloride for (1), (2) and (5), and a solution of ammonium chloride for the other tests.]

**(Instructions for performance of tests (1) and (2), see p. 78).**

(1) The dry salt gives **no reaction** with **dilute hydrochloric acid.**

(2) The dry salt **effervesces** with **concentrated sulphuric acid,** evolving hydrogen chloride, a *colourless gas* which *fumes strongly* when it meets the air, and *reddens* a *moistened blue litmus* paper.

*Note.*—Most chlorides give this reaction at once with cold strong sulphuric acid. Some require that the mixture should be warmed. It is difficult to obtain HCl gas from *mercurous* or *stannous* or *lead* chloride. Special care must be taken when either of these metallic radicals is known to be present.

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *white* curdy precipitate of silver chloride, AgCl, which is *insoluble in cold dilute nitric acid.* [For other properties of AgCl, see p. 15.]

(4) The (neutral) *solution* gives, with **barium chloride** solution, *no precipitate.*

(5) Mix about a gramme of the *dry salt* with the same amount of **manganese dioxide,** put the mixture into a small *dry* test-tube, add enough **water** to make a thick paste and drop in about 1 cc. of **strong sulphuric acid.** *Chlorine gas* is evolved, recognizable by its yellow-green *colour*, its suffocating *smell* and its power of *bleaching* a piece of *wet red litmus* paper.

*Notes.*—(i) The wet litmus paper must simply be held in the gas, not dipped into the mixture. It must become quite *white.*

(ii) The reactions involved are (*a*) formation of HCl from the chloride and sulphuric acid, (*b*) oxidation of this HCl by the $MnO_2$ :—

$$\begin{cases} MnO_2 + H_2(SO_4) = Mn(SO_4) + H_2O + [O] \\ 2HCl + [O] = H_2O + Cl_2. \end{cases}$$

(iii) There are two chlorides which will not give this reaction, *mercurous* and *stannous* chlorides. When the metallic radical is known to be $Hg^{\cdot\cdot}$ or $Sn^{\cdot\cdot}$ *mix the original salt with powdered potassium bichromate and strong sulphuric acid* (*no water*), *and heat. Chlorine* will then be evolved and can be recognized by its *smell* and *bleaching-powder.* The bichromate is a more powerful oxidizing agent than maganese dioxide. A red volatile liquid, chromyl chloride, $CrO_2Cl_2$, is also formed along with the chlorine.

## XXIX.

### **Hydrobromic Acid** and **Bromides.**

Formula of acid, **HBr.** **Monobasic.**

The compound HBr, hydrogen bromide, is a gas, extremely soluble in water. It is to this solution in water that the name hydrobromic acid is applied.

**Examples of salts:—**

| | |
|---|---|
| Potassium bromide | KBr |
| Magnesium bromide | $MgBr_2$ |
| Aluminium bromide | $AlBr_3$. |

**Solubility of salts.**—The bromides closely resemble the chlorides (q.v.).

### **Reactions of Bromides.**

[Use dry potassium bromide for (1), (2) and (5), and a solution of this salt for the other tests.]

(1) The dry salt gives **no reaction** with **dilute hydrochloric acid.**

(2) The dry salt **effervesces** with **concentrated sulphuric acid** evolving **both** hydrogen bromide, a *colourless gas* which *fumes strongly* when it meets the air, turning *wet blue litmus* paper *red*, **and** bromine vapour, recognized by its *orange colour.*

*Notes.*—(i) The majority of bromides give this reaction at once with cold strong sulphuric acid. Some require that the mixture should be warmed. It is characteristic that *the liquid is orange-red* from presence of free bromine.

(ii) The production of the free bromine is due to the fact that strong sulphuric acid behaves towards HBr as an oxidizing agent:—

$$H_2(SO_4) = H_2O + SO_2 + [O]$$
$$2HBr + [O] = H_2O + Br_2.$$

(3) The (neutral) *solution* gives, with **silver nitrate** solu-

tion, a *very pale yellow* curdy precipitate of silver bromide, AgBr, which is *insoluble in cold dilute nitric acid.*

*Note.*—Precipitated silver bromide is also, like the chloride, soluble in ammonia solution but not quite so easily.

(4) The (neutral) *solution* gives, with **barium chloride** solution, *no precipitate.*

(5) On testing a bromide in the manner described under reaction No. (5) for chlorides (see above) **bromine vapour** is evolved, recognizable by its orange-red *colour*, its suffocating and irritating *smell* (it is *dangerous* to inhale bromine vapour) and its *bleaching power.*

*Note.*—Certain bromides, e.g. $Hg_2Br_2$ or $PbBr_2$, evolve bromine better with bichromate and strong sulphuric acid as described in Note (iii) under reaction No. (5) for chlorides.

(6) The *solution* of a bromide treated with a very little **chlorine water** is coloured *orange* by separated bromine and if a little **carbon disulphide** (about half a cc.) be shaken up with this solution, the $CS_2$ dissolves the bromine and, on standing, sinks to the bottom, as an *orange-coloured globule.*

*Note.*—Chlorine expels bromine from bromides, taking its place to form chlorides. But care must be taken not to add too much of the chlorine solution, for chlorine can combine with free bromine to form a compound which has not the characteristic colour of bromine.

## XXX.

## **Hydriodic Acid** and **Iodides.**

Formula of acid, **HI**. **Monobasic.**

The compound HI, hydrogen iodide, is a gas, extremely soluble in water. It is to this solution in water that the name hydriodic acid is applied.

**Examples of salts** :—

| | |
|---|---|
| potassium iodide | KI |
| cadmium iodide | $CdI_2$ |
| aluminium iodide | $AlI_3$. |

**Solubility of salts.**—The iodides closely resemble the chlorides (q.v.), but are, as a class, less easily soluble. Thus the iodide of bismuth, $BiI_3$, can be precipitated as a black powder from strong solutions of bismuth salts, while mercuric iodide, $HgI_2$ (see p. 24) is also insoluble. The insoluble iodides, however, dissolve for the most part in excess of potassium iodide solution, forming soluble 'double salts.' Thus $HgI_2$ gives the *colourless* soluble $KHgI_3$ and $BiI_3$ the orange-coloured soluble $KBiI_4$.

## Reactions of Iodides.

[Use dry potassium iodide for (1), (2) and (5) and a solution of this salt for the other tests.]

(1) The dry salt gives **no reaction** with **dilute hydrochloric acid.**

(2) The dry salt **effervesces** with **concentrated sulphuric acid** evolving **both** hydrogen iodide, a *colourless, fuming, acid* gas **and** iodine itself, recognizable by the *violet colour* of its vapour and the condensation of this upon the sides of the tube to an almost black solid.

*Notes.*—(i) Most iodides give the reaction at once with cold strong sulphuric acid. But *the iodides of mercury will not give it,* and that of lead does so with difficulty, on heating.

(ii) The production of free iodine is due to the fact that HI reduces strong sulphuric acid, being itself oxidized :—

$$H_2(SO_4) = H_2O + SO_2 + [O]$$
$$2HI + [O] = H_2O + I_2.$$

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *yellow* curdy precipitate of silver iodide, AgI, which is *insoluble in cold dilute nitric acid.*

*Note.*—Precipitated silver iodide is, unlike the chloride and bromide, *insoluble in ammonia solution.*

(4) The (neutral) *solution* gives, with **barium chloride** solution, *no precipitate.*

(5) On testing an iodide in the manner described under reaction (No. 5.) for chlorides (see above) *iodine* is evolved

recognizable by the *violet colour* of the vapour and by its condensing upon the walls of the tube.

*Note.*—With the *iodides of mercury,* and preferably also with that of lead, this reaction must be carried out as described in Note (iii), Reaction (5) of chlorides, with potassium bichromate and strong sulphuric acid.

(6) A *solution* of an iodide treated with **chlorine water** and **carbon disulphide** as described under reaction (No. 6) of bromides (see above), is coloured *brown* by separated iodine which dissolves in the $CS_2$ and gives a *violet coloured globule.*

*Note.*—It is essential that the chlorine should *not* be added in excess, since chlorine can combine with iodine to give iodine chloride which, in solution, is colourless.

## XXXI.

### **Hydrocyanic Acid** and **Cyanides.**

Formula of Acid, **H(CN).** **Monobasic.**

The compound H(CN), hydrogen cyanide, is a volatile, colourless liquid. Its solution in water is known as hydrocyanic acid, and, commonly, as 'prussic acid.'

**N.B.—All cyanides are POISONOUS. Handle them in small quantities and with care.**

**Examples of Salts:—**

| | |
|---|---|
| Potassium cyanide | K(CN) |
| Nickel cyanide | $Ni(CN)_2$. |

**Solubility of salts.**—The *cyanides,* as a class, are *insoluble in water.* Those of potassium and sodium are soluble and so are those of barium, strontium and calcium. Mercuric cyanide is also soluble in water, but it behaves anomalously, not showing *all* the reactions either of mercuric salts or of cyanides. The insoluble cyanides as a rule dissolve in a solution of potassium cyanide to form various 'double salts,' some of which—like the ferro- and ferricyanides discussed below—are exceedingly stable compounds.

## Reactions of Cyanides.

[Use dry nickel cyanide for (1), (2) and (5) and a solution of potassium cyanide (freshly-made in *cold* water) for the rest.]

(1) The dry salt gives *no visible reaction* with **dilute hydrochloric acid** but more or less hydrocyanic acid, recognizable by its powerful *smell of bitter almonds*, is set free.

*Note*.—With a soluble cyanide, like K(CN), this reaction is *very marked* indeed and care is needed *not to inhale* the H(CN) which is a dangerous substance.

With nickel cyanide, and other such insoluble ones, only traces of H(CN) are evolved, even on warming with the dilute hydrochloric acid.

(2) The dry salt is acted upon by **concentrated sulphuric acid** on warming, the mixture effervesces briskly and *carbon monoxide* (recognizable by its burning with a blue flame when lighted) is evolved.

*Notes*.—(i) With potassium cyanide this effervescence takes place while the strong sulphuric acid is cold and the CO is mixed with a certain amount of H(CN).

(ii) The action of the strong sulphuric acid is two-fold (*a*) it liberates prussic acid,

$$(\text{cyanide}) + H_2(SO_4) = 2H(CN) + (\text{sulphate}),$$

(*b*) it causes this H(CN) to combine with hydrogen and oxygen, from water present in the acid,

$$H(CN) + H_2O = NH_3 + CO,$$

the final products of this part of the change being ammonium sulphate and carbon monoxide.

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *white precipitate* of silver cyanide, Ag(CN), *which is insoluble in cold dilute nitric acid.*

*Note*.—This precipitate, of Ag(CN), is distinguished from the very similar precipitate of the chloride, AgCl, by the fact that it (the cyanide) is readily soluble in excess of the original solution. This may easily be seen by adding the silver nitrate solution gradually, when the precipitate formed will, at first, disappear on shaking. It will only be permanent after a slight excess of the silver nitrate has been added.

(4) The (neutral) *solution* gives, with **barium chloride** solution *no precipitate.*

*Note*.—This is only true if the cyanide in question is pure. Much of the commercial potassium cyanide contains potassium carbonate, and in that case more or less of the white barium carbonate will be precipitated.

(5) If a small portion of **any cyanide,** soluble or insoluble, be **boiled** for a few minutes with a few ccs. of **yellow ammonium sulphide** solution, a reaction occurs by which a **sulphocyanide** is produced. The liquid is filtered, if not clear, and the filtrate is evaporated (in the fume-cupboard!) **just** *to dryness.* The residue, treated with **ferric chloride** solution, will give the characteristic *blood-red* colour of ferric sulphocyanide.

N.B.—Some metallic cyanides evolve cyanogen gas when they are heated e.g. $Hg(CN)_2$, $Ag(CN)$, $Ni(CN)_2$.

## XXXII.

## Sulphuretted Hydrogen (*Hydrosulphuric Acid*) *and* Sulphides.

Formula of Acid, **$H_2S$.** **Dibasic.**

The compound $H_2S$, hydrogen sulphide, is a gas of characteristic and disagreeable odour, which is somewhat soluble in water. Its solution is feebly acid and is sometimes described as hydrosulphuric acid.

**Examples of Salts** :—

| | |
|---|---|
| Sodium sulphide | $Na_2S$ |
| Zinc sulphide | $ZnS$ |
| Antimony sulphide | $Sb_2S_3$ |
| Stannic sulphide | $SnS_2$. |

**Solubility of salts.**—As we have already seen in our study of the metals, *the sulphides,* as a class, are *insoluble salts,* many of them being insoluble not only in water but also in dilute acids. The sulphides of potassium and sodium (and of ammonium) are soluble in water. Those of aluminium and chromium, as well as of barium, strontium, calcium and magnesium, are more or less easily decomposed by water, especially if warmed, yielding $H_2S$ and the hydroxides of these metals.

## Reactions of Sulphides.

[Use powdered antimony sulphide for (1), (2) and (5) and a solution of sodium sulphide for the rest.]

(1) The dry salt treated with **dilute hydrochloric acid** yields, on warming, *hydrogen sulphide*, a colourless gas recognizable by its fœtid *smell* and by its power of, *blackening* a paper moistened with *alkaline solution of lead hydroxide* (see note).

*Notes.*—(i) An *alkaline solution of lead hydroxide* is prepared by adding to a small quantity of lead acetate or lead nitrate a solution of potassium (or sodium) hydroxide until the precipitate at first formed is re-dissolved. It is a most sensitive reagent for $H_2S$, yielding with this gas the black lead sulphide, PbS.

(ii) Some sulphides, such as those of mercury, silver, copper, &c., are hardly attacked at all by dilute hydrochloric acid, even hot. It is well to repeat the experiment, if a sulphide be suspected, using strong hydrochloric acid. This acts upon them more readily. The sulphides of arsenic, realgar, $As_2S_2$ and orpiment, $As_2S_3$, are not attacked even by strong hydrochloric acid. Their colours are characteristic, and if they be suspected test (5) below should be applied.

(2) The dry salt, with **concentrated sulphuric acid** seldom gives any characteristic reaction since any $H_2S$ which is liberated reacts with the sulphuric acid, particularly when warm, to give sulphur dioxide and sulphur :—

$$H_2(SO_4) + H_2S = 2H_2O + SO_2 + S.$$

(see the remarks in *Note* (iii) on p. 78 above).

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *black* precipitate of silver sulphide, $Ag_2S$, which is *insoluble in cold dilute nitric acid.*

(4) The (neutral) solution gives, with **barium chloride** solution, *no precipitate.*

(5) If any insoluble sulphide (and this test is not necessary with soluble sulphides) be melted together with (solid) sodium (or potassium) hydroxide it is more or less decomposed and some sodium (or potassium) sulphide is formed. On letting the melt cool and adding cold water a solution is obtained which contains alkali sulphide. If this *dilute* solution, filtered from any insoluble residue, be added to an alkaline lead hydroxide solution (see *Note* (i) to Reaction (1) above), a black precipitate of lead sulphide is formed.

N.B.—Some sulphides volatilize (and sublime) when heated, e.g. HgS, $As_2S_3$ (see Chapter VI).

For other acids of Group I, ferrocyanic, ferricyanic, sulphocyanic and hypochlorous (see Chapter IV below).

## ACIDS OF GROUP II.

### XXXIII.

### Acetic Acid and Acetates.

Formula of acid, $\mathbf{H(C_2H_3O_2)}$. **Monobasic.**

Acetic acid itself is a colourless liquid which boils at 118 C. and freezes at 17°C. It is thus solid in cold weather ('glacial acetic acid'). It is readily soluble in water. It possesses a peculiar and very characteristic smell.

**Examples of Salts:—**

Sodium acetate $Na(C_2H_3O_2)$
Lead acetate $Pb(C_2H_3O_2)_2$.

**Solubility of Salts.**—The *acetates* as a class are *soluble in water.* The silver salt (see below) is but sparingly soluble in cold water.

### Reactions of Acetates.

[Use dry sodium acetate for (1), (2) and (5) and a solution of this salt for (3), (4) and (6).]

(1) The dry salt gives no visible reaction with **dilute hydrochloric acid** but, especially on warming, the characteristic *smell* of *acetic acid* is noticeable.

(2) The dry salt gives no visible reaction with **concentrated sulphuric acid** but on warming *acetic acid* vapour is evolved which is recognizable by its *smell.*

*Note.*—If the sulphuric acid is over-heated the smell of the sulphur trioxide evolved will entirely mask that of the acetic acid. The acetic acid vapour is combustible, and if enough be allowed to accumulate in the tube it may be burned, giving a blue flame.

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *crystalline, white* precipitate of silver acetate, $Ag(C_2H_3O_2)$, which is *very easily soluble in cold dilute nitric acid.*

*Note.*—The precipitate of silver acetate may, if the acetate solution be somewhat dilute, form slowly. It will come down abundantly on rubbing the walls of the test-tube gently with a glass rod.

(4) The (neutral) *solution* gives *no precipitate* with **barium chloride** solution.

*Note.*—Remember that, if the metallic radical of the salt be *lead,* barium *nitrate* must be used here instead of the chloride (see p. 79).

(5) About 1 gramme of a powdered solid acetate is treated with 1 to 2 ccs. of **absolute alcohol** and an equal volume of **concentrated sulphuric acid** is added gradually, the whole being well mixed. On warming the mixture ethyl acetate (acetic ester) is formed which is recognized by its characteristic smell, resembling that of a freshly-cut apple.

*Notes.*—(i) The reactions involved are (*a*) formation of acetic acid :—(acetate) + $H_2(SO_4)$ = (sulphate) + $2H(C_2H_3O_2)$; (*b*) reaction of this acetic acid with the alcohol :—

$$H(C_2H_3O_2) + C_2H_5(OH) = H_2O + C_2H_5(C_2H_3O_2).$$

(ii) This test may be varied and made more striking by substituting amyl alcohol, $C_5H_{11}(OH)$, [fusel oil] for the absolute alcohol. In that case amyl acetate is produced which has a very powerful odour resembling that of ‘pear drops.’

(6) The (neutral) *solution* treated with a *few drops* (only) of **ferric chloride** solution acquires a *red colour,* due to the formation of ferric acetate. If this solution be diluted with water and then boiled a *brown precipitate* is formed, consisting of basic acetate of iron :—

$$\left\{\begin{array}{l}(\text{acetate}) + FeCl_3\,aq. = (\text{chloride}) + Fe(C_2H_3O_2)_3\,aq.\\ Fe(C_2H_3O_2)_3\,aq. + 2H_2O = 2H(C_2H_3O_2) + Fe(C_2H_3O_2)(OH)_2.\end{array}\right.$$

N.B.—Acetates when heated evolve combustible vapours.

## XXXIV.

### Nitrous Acid and Nitrites.

Formula of Acid, $\mathbf{H(NO_2)}$. **Monobasic.**

The compound $H(NO_2)$ has never been isolated. When it is formed in any reaction it decomposes at once :—

$$2H(NO_2) = H_2O + N_2O_3$$

and the nitrous anhydride, $N_2O_3$, in its turn decomposes into nitric oxide and nitrogen peroxide :—

$$N_2O_3 = NO + NO_2.$$

The unstable $N_2O_3$ has, when dissolved in water, a distinct *blue* colour and the mixture of NO and $NO_2$ gases which it evolves, has, of course, the *reddish-brown* colour of nitrogen peroxide.

**Examples of Salts** :—

| | |
|---|---|
| Sodium nitrite | $Na(NO_2)$ |
| Barium nitrite | $Ba(NO_2)_2$. |

**Solubility of salts**.—All *nitrites* are *soluble in water* though the silver salt (see below) is almost insoluble in *cold* water.

### Reactions of Nitrites.

[Use dry powdered sodium nitrite for (1) and (2) and a fresh solution of this salt in cold water for the rest].

(1) The dry salt *effervesces* briskly when treated with **dilute hydrochloric acid**, a *reddish-brown gas* (containing nitrogen peroxide, $NO_2$) being evolved, while the solution from which this gas is coming shows a distinct *blue* tinge.

(2) The action of **concentrated sulphuric acid** is in all essentials similar but it is more violent, and is complicated by the fact that $H_2(SO_4)$ reacts with $N_2O_3$ to form nitrosyl hydrogen sulphate

$$N_2O_3 + 2H_2(SO_4) = 2(NO)H(SO_4) + H_2O.$$

**Strong sulphuric acid should not be used as a reagent for nitrites.** The *characteristic reaction with dilute hydrochloric acid is more marked and affords ample evidence.*

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *white, crystalline precipitate* of silver nitrite, $Ag(NO_2)$, which is *readily soluble in cold dilute nitric acid.* The addition of the dilute nitric acid not only dissolves the precipitate but also liberates nitrous fumes.

(4) The (neutral) *solution* gives *no precipitate* with **barium chloride** solution.

(5) If a solution of a nitrite be placed in a test-tube, and a solution of **ferrous sulphate**, acidified with a little *acetic acid*, be poured in so as to form a layer upon the top of the nitrite solution, a *brown ring* is formed where the two liquids meet.

*Notes.*—(i) This brown ring is composed of a compound of ferrous sulphate with nitric oxide. The acetic acid liberates nitrous acid, which then yields nitric oxide (as explained above), and the nitric oxide combines with the ferrous sulphate to a dark-coloured compound $FeSO_4.NO$.

(ii) This test must be carefully distinguished from the similar but quite distinct test for *nitrates* described below. Here dilute acetic acid only is required, but in the nitrate test concentrated sulphuric acid is needed.

(6) If a solution of **potassium iodide** be treated with **one drop** of a solution of a nitrite, and a few drops of **acetic acid** be added, the mixture will become *brown* owing to separation of iodine. On adding a drop of this brown liquid to some **starch** solution (or starch-paste) the dark blue iodide of starch will be formed.

*Note.*—The nitrous acid, set free from the nitrite by the acetic acid, here acts as an *oxidizing agent,*

$$\begin{cases} 2H(NO_2) = H_2O + 2NO + [O] \\ 2KI + H_2O + [O] = 2KOH + I_2. \end{cases}$$

For other acids of Group II, formic and cyanic acids, see Chapter IV below.

## ACIDS OF GROUP III.

### XXXV.

### **Carbonic Acid** and **Carbonates.**

Formula of Acid, $\mathbf{H_2(CO_3)}$. **Dibasic.**

The compound $H_2(CO_3)$ has never been isolated. When it is produced in a reaction it decomposes at once :—

$$H_2(CO_3) = H_2O + \mathit{CO_2}$$

and carbon dioxide (or carbonic anhydride) is evolved as a gas. Carbon dioxide is somewhat soluble in cold water, and the solution has a feebly acid reaction, but all the gas is expelled on heating the solution.

**Examples of Salts**:—

| | |
|---|---|
| Sodium bicarbonate (acid salt) | $NaH(CO_3)$ |
| Sodium carbonate | $Na_2(CO_3)$ |
| Calcium carbonate | $Ca(CO)_3$. |

**Solubility of salts.**—The *carbonates* as a class are *insoluble in water.* Those of sodium, potassium and ammonium are soluble, and the bicarbonates of these metallic radicals are less soluble than their carbonates. The carbonates of barium, calcium, magnesium, etc. are insoluble in water, but they dissolve very slightly in water which contains $CO_2$ in solution, forming the bicarbonates of those metals, e. g. :—

$$Ca(CO_3) + [H_2O + CO_2] = Ca[H(CO_3)]_2.$$

This is one of the causes of 'hardness' in waters. When the solution of a bicarbonate is boiled the salt is decomposed and the carbonate is formed, with evolution of carbon dioxide :—

$$Ca[H(CO_3)]_2 = CaCO_3 + [H_2(CO_3)]$$
$$[H_2(CO)_3] = H_2O + CO_2.$$

Thus 'hard' waters which owe their 'hardness' to the dissolved bicarbonates of calcium or magnesium are made 'soft' by boiling and their 'hardness' is described as '*temporary*.'

## Reactions of Carbonates.

[Use powdered calcium carbonate for (1) and a solution of sodium carbonate for (3) and (4).]

(1) The dry salt *effervesces* when treated with **dilute hydrochloric acid,** evolving carbon dioxide as a *colourless gas,* which can be easily identified by closing the tube with the thumb till the gas has accumulated under slight pressure, and then allowing it to shoot into another tube which contains clear *lime-water* (calcium hydroxide solution), and shaking this up. The *lime-water* is *turned milky* owing to formation of calcium carbonate :—

$$Ca(OH)_2 + CO_2 = Ca(CO_3) + H_2O.$$

(2) The action of **concentrated sulphuric acid,** so far as it acts at all, is similar, but this acid acts very sluggishly and *strong sulphuric acid should not be used as reagent when the action of dilute hydrochloric acid has proved that a carbonate is present.*

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *white precipitate* of silver carbonate, $Ag_2(CO_3)$, which is *easily soluble,* with effervescence, *in cold dilute nitric acid.*

(4) The (neutral) *solution* gives, with **barium chloride** solution, a *white precipitate* of barium carbonate, $Ba(CO_3)$, which is *easily soluble,* with effervescence, *in cold dilute nitric acid.*

*Note.*—When the metallic radical of a salt is found to be potassium or sodium and the acid radical that of a carbonate, it is necessary to distinguish the salt as a carbonate or bicarbonate. To do this a portion of the salt is *heated with water* If it be a bicarbonate, carbon dioxide will be evolved with (slight) effervescence :—

$$2KH(CO_3) = K_2CO_3 + H_2O + CO_2.$$

## XXXVI.

## Sulphurous Acid and Sulphites.

Formula of Acid, $\mathbf{H_2(SO_3)}$ **Dibasic.**

The compound $H_2(SO_3)$ has not been isolated. When it is produced in a chemical reaction it decomposes, especially on gentle warming, evolving sulphur dioxide (sulphurous anhydride) $SO_2$ :—

$$H_2(SO_3) = H_2O + SO_2.$$

Sulphur dioxide is soluble in cold water, and the solution has an acid reaction, but all the gas is driven off on heating the solution.

**Examples of Salts** :—

| | |
|---|---|
| Sodium bisulphite (acid salt) | $NaH(SO_3)$ |
| Sodium sulphite | $Na_2(SO_3)$ |
| Lead sulphite | $Pb(SO_3)$. |

**Solubility of salts.** — The *sulphites* as a class are *insoluble in water*. Those of potassium and sodium however dissolve easily.

### Reactions of Sulphites.

[Use powdered solid sodium sulphite for (1) and a freshly made solution of this salt for the rest.]

(1) The dry salt treated with **dilute hydrochloric acid** dissolves in it without noticeable effervescence, but if the solution be *warmed gently* an *effervescence* is observed, with evolution of *sulphur dioxide*, $SO_2$, a colourless gas recognizable by its pungent odour of burning sulphur. The gas can be further identified by allowing it to accumulate in the tube, as described under reaction No. (1) for carbonates, and then transferring it to a tube containing a *small* quantity of *potassium chromate* solution *acidified with dilute hydrochloric acid.* On shaking with the gas the *orange* colour of this mixture is changed to *green.*

*Note.*—The chromate here acts as an oxidizing agent :—

$$2K_2(CrO_4) + 10HCl = 4KCl + 2CrCl_3 + 5H_2O + [3O]$$

and the sulphur dioxide and water ( = sulphurous acid) as reducing agent :—

$$3SO_2 + 3H_2O + [3O] = 3H_2(SO_4).$$

The chromium chloride solution is green.

(2) The dry salt with **concentrated sulphuric acid** would give the same reaction, *but the production of $SO_2$ when using strong $H_2(SO_4)$ would not be valid evidence of the presence of a sulphite, for the sulphur dioxide* **might** *be derived from the sulphuric acid.* **Strong sulphuric acid must not be used as a reagent when the action of dilute hydrochloric acid has revealed the presence of a sulphite.**

(3) The (neutral) *solution*, treated with **silver nitrate** solution, gives a *white precipitate* of silver sulphite, $Ag_2(SO_3)$, which is *easily soluble in cold dilute nitric acid.*

(4) The (neutral) *solution* gives, with **barium chloride** solution, a *white precipitate* of barium sulphite, $Ba(SO_3)$, which is *readily soluble in cold dilute nitric acid.*

*Note.*—Solutions of sulphites somewhat rapidly absorb oxygen from the air, and yield sulphates :—

$$Na_2(SO_3) + [O] = Na_2(SO_4).$$

Now barium sulphate is insoluble in dilute nitric acid, and so it frequently happens that the precipitate given by sulphite solutions with $BaCl_2$ aq. is not *wholly* dissolved by dilute nitric acid. It is easy, however, to see that most of it is soluble.

(5) If to a very dilute solution of **potassium permanganate, acidified with dilute sulphuric acid,** a small quantity of a sulphite (either solid or dissolved in water) be added, the *purple colour* of the permanganate is *discharged* and the solution becomes colourless.

*Note.*—This decolourization of the permanganate is due to the action of that salt as an oxidizing agent :—

$$2K(MnO_4) + 3H_2(SO_4) = K_2(SO_4) + 2Mn(SO_4) + 3H_2O + [5O]$$

the oxygen being appropriated by the sulphurous acid (or $SO_2 + H_2O$) which thus behaves as a reducing agent :—

$$5H_2(SO_3) + [5O] = 5H_2(SO_4),$$

while the purple permanganate is changed into the practically colourless manganese sulphate.

## XXXVII.

### **Oxalic Acid** and **Oxalates.**

Formula of acid, $\mathbf{H_2(C_2O_4)}$ **Dibasic.**

Oxalic acid is a white crystalline solid, readily soluble in water to an acid solution. The crystals ordinarily contain two molecules of water of crystallization, $H_2(C_2O_4).\ 2H_2O$.

**Examples of salts:—**

| | |
|---|---|
| Potassium hydrogen oxalate (acid salt) | $KH(C_2O_4)$ |
| Ammonium oxalate | $(NH_4)_2(C_2O_4)$ |
| Calcium oxalate | $Ca(C_2O_4)$. |

**Solubility of salts.**—The *oxalates* as a class are *insoluble in water.* The ammonium salts, and those of potassium and sodium are, however, soluble.

### Reactions of Oxalates.

[Use calcium oxalate for (1), (2) and (6), and a solution of ammonium oxalate for the rest.]

(1) The dry salt treated with **dilute hydrochloric acid** merely dissolves giving *no effervescence* and *no characteristic reaction.*

(2) The dry salt, with **concentrated sulphuric acid,** gives no reaction while cold but, *on heating, effervesces briskly* evolving **both** *carbon dioxide* (lime-water test) **and** *carbon monoxide* (burns with a blue flame when lighted).

Note.—Test for carbon dioxide (as described under Reaction No. 1 of Carbonates) first, and afterwards for carbon monoxide. The reverse order would be illogical, for carbon monoxide yields carbon dioxide when it burns. It frequently happens that all the oxalate taken is destroyed while the test for $CO_2$ is being carried out, and it is then necessary to take a fresh portion of salt in order to find the CO. The effervescence will continue for some time after the tube is withdrawn from the flame. The reaction that occurs is the withdrawal, by the hot strong sulphuric acid, of the elements of water from the oxalic acid set free:—

$$\left\{\begin{array}{l}\text{(oxalate)} + H_2(SO_4) = \text{(sulphate)} + H_2(C_2O_4)\\ H_2(C_2O_4) - H_2O = CO_2 + CO.\end{array}\right.$$

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *white precipitate* of silver oxalate, $Ag_2(C_2O_4)$, which *is soluble* (though not very easily) *in cold dilute nitric acid.*

(4) The (neutral) *solution* gives, with **barium chloride** solution, a *white precipitate* of barium oxalate, $Ba(C_2O_4)$, readily *soluble cold dilute nitric acid.*

(5) If an oxalate (solid or in solution) be added to **dilute sulphuric acid** and the mixture be **heated nearly to boiling**, the addition of a little **manganese dioxide** will produce a *brisk effervescence* with *evolution of carbon dioxide* (lime-water test).

*Note.*—In this reaction the oxalic acid (set free from the oxalate by the dilute sulphuric acid) behaves as a reducing agent

$$MnO_2 + H_2(SO_4) = Mn(SO_4) + H_2O + [O]$$
$$H_2(C_2O_4) + [O] = H_2O + 2CO_2.$$

N.B.—(i) Oxalates are decomposed when heated alone. Those of the alkali metals, and of magnesium, calcium, strontium and barium, evolve carbon monoxide and are transformed into carbonates which may be recognized by their effervescence with acids (after cooling). Those of other metals such as iron, nickel, cobalt, copper, leave a residue of the metal itself (see Chapter VI).

(ii) When a soluble oxalate has been detected it should be determined whether it is a neutral or an acid salt. The reaction of the solution to litmus will indicate which, and, further, a solution of an *acid* oxalate will give a brisk effervescence with sodium carbonate solution.

## XXXVIII.

### **Tartaric Acid** and **Tartrates.**

Formula of acid, $\mathbf{H_2(C_4H_4O_6)}$. **Dibasic.**

Tartaric acid is a white crystalline solid, readily soluble in water, giving an acid solution.

**Examples of salts :—**

| | |
|---|---|
| Potassium hydrogen tartrate (acid salt)<br>('Cream of Tartar') | $KH(C_4H_4O_6)$ |
| Potassium tartrate | $K_2(C_4H_4O_6)$ |
| Calcium tartrate | $Ca(C_4H_4O_6)$. |

*Note.*—Recall also 'tartar emetic' or antimonyl potassium tartrate $K(SbO)(C_4H_4O_6)$—(see p. 38), and notice the well-known Rochelle Salt which is potassium sodium tartrate $KNa(C_4H_4O_6)$.

**Solubility of salts.**—The *tartrates* as a class are *insoluble in water.* Those of ammonium and of the alkali metals are soluble however, though the acid potassium salt is very sparingly so (see p. 74).

### Reactions of Tartrates.

[Use powdered 'Cream of Tartar' for (1), (2) and (6) and a solution of 'Rochelle salt' for the rest.]

(1) The dry salt treated with **dilute hydrochloric acid** gives *no reaction.*

(2) The dry salt, with **concentrated sulphuric acid,** remains unaffected while cold, but, on **heating,** rapidly *darkens* and soon becomes *quite black.*

*Note.*—This *charring* is most characteristic and serves to distinguish tartrates from all the other salts we shall have to deal with.

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *white precipitate* of silver tartrate, $Ag_2(C_4H_4O_6)$, which is very easily *soluble in cold dilute nitric acid.*

(4) The (neutral) *solution* gives, with **barium chloride** solution, a *white precipitate* of barium tartrate, $Ba(C_4H_4O_6)$, which is easily *soluble in cold dilute nitric acid.*

(5) If **silver nitrate** solution be added to a neutral solution of a tartrate and then **very dilute ammonia** solution be dropped in until the precipitate of silver tartrate is nearly (but *not quite*) dissolved, and the whole be now gently heated for some time, a *mirror of metallic silver is deposited* upon the walls of the tube.

*Notes.*—(i) This is an example of the action of tartrates as *reducing* agents (compare p. 16).

(ii) In case a tartrate soluble in water gives an acid solution, it must, of course, be neutralized before applying this test (or Nos. 3 and 4).

(iii) If too much ammonia has, by accident, been added so that the solution has become clear, more silver nitrate must be added to make it turbid again.

(iv) This 'silver mirror test' is also applicable to tartrates insoluble in water (which cannot give tests 3 and 4, therefore) for, if such insoluble tartrates be boiled for some time with sodium carbonate solution, and the resulting liquid be filtered off, some sodium tartrate is obtained in solution, and, on now adding silver nitrate and ammonia as above, the test can be carried out.

(v) The formation of the mirror proceeds faster if, after the reagents have been added as above, a single drop of sodium (or potassium) hydroxide solution is also added before the tube is warmed.

(6) Any tartrate when **heated by itself** *chars*, darkening in colour and giving a *smell resembling that of burnt sugar.*

## XXXIX.

## Boric Acid and Borates.

Formula of acid, $\mathbf{H_3(BO_3)}$ (salts not known)
and $\mathbf{H(BO_2)}$ **Monobasic.**

Boric acid forms colourless lustrous crystals of the composition $H_3(BO_3)$. These are not very soluble in cold water, and the solution has a weakly acid reaction. When these crystals are heated to 100°C, water is given off and $H(BO_2)$ remains as a white solid :—

$$H_3(BO_3) = H_2O + H(BO_2).$$

The acid $H_3(BO_3)$, which may be regarded simply as the hydroxide of boron, $B(OH)_3$, is known as *orthoboric acid.* No corresponding salts are known. The acid derived from this by loss of water, $H(BO_2)$, is known as *metaboric acid.* It is monobasic, and most of the borates are 'metaborates' derived from it. But the commonest of all borates, that of sodium, usually known as *borax*, is not even a metaborate. It is derived from an acid formed when *metaboric acid*, $H(BO_2)$, is heated to 160°C, a further loss of water taking place thus:—

$$4H(BO_2) = H_2O + H_2(B_4O_7).$$

The acid $H_2(B_4O_7)$ is known as *pyroboric acid*, and borax is the sodium pyroborate $Na_2(B_4O_7)$ crystallised with $10H_2O$. This water (of crystallisation) is all driven off on heating.

All borates give the same reactions, those of metaborates.

**Examples of salts** :—

| | |
|---|---|
| Sodium pyroborate | $Na_2(B_4O_7)$ |
| Manganese borate | $Mn(BO_2)_2$. |

**Solubility of salts.**—The *borates* are, as a class, *insoluble in water*, but those of sodium and potassium dissolve in that solvent. (The solutions have an alkaline reaction).

## Reactions of Borates.

[Use powdered borax for (1), (2) and (5), and a solution of borax in water for the rest.]

(1) The dry salt gives *no reaction* with **dilute hydrochloric acid.**

(2) The dry salt gives *no reaction* with **concentrated sulphuric acid.**

(3) The (aqueous) *solution* gives, with **silver nitrate** solution, a white precipitate of silver *metaborate*, $Ag(BO_2)$:—

$$Na_2(B_4O_7) + 2Ag(NO_3) + 3H_2O = 2Na(NO_3) + 2Ag(BO_2) + 2H_3(BO_3)$$

which is *very readily soluble in cold dilute nitric acid.*

(4) The (aqueous) *solution* gives, with **barium chloride** solution, a *white precipitate* of barium *metaborate*, $Ba(BO_2)_2$ :—
$Na_2(B_4O_7) + BaCl_2 + 3H_2O = 2NaCl + Ba(BO_2)_2 + 2H_3(BO_3)$
which is *easily soluble in cold dilute nitric acid.*

> *Note.*—This precipitate is also *soluble in excess of barium chloride solution*, so care must be taken not to add too much of the reagent.

(5) If any borate be **dissolved in dilute hydrochloric acid**, and a drop of this solution be placed upon a strip of **turmeric paper** and the paper be then carefully and thoroughly **dried**, a *red* stain is produced upon the paper. If this red stain be now moistened with sodium (or potassium) hydroxide solution it becomes *dark bluish-black.*

> *Note.*—The reactions occurring are not known. The red (really a purple-red) colour is a product of the action of boric acid upon the yellow turmeric. Boric acid is not the only acid which will give a distinctive colour to turmeric, but the others which will do so are far from common and we have not to consider any of them.

*Note.*—There is also a very characteristic 'flame test' for boric acid, which is described below (Chapter VI).

Other acids belonging to Group III—iodic, pyrophosphoric and metaphosphoric, are dealt with in Chapter IV below.

## ACIDS OF GROUP IV.

### XL.

### **Phosphoric Acid** and **Phosphates.**

Formula of acid $\mathbf{H_3(PO_4)}$ **Tribasic.**

The compound $H_3(PO_4)$, known as *orthophosphoric acid*, is a low-melting crystalline solid, very soluble in water. The concentrated solution is syrupy. When the $H_3(PO_4)$ is heated, it loses water and finally, at a red-heat *metaphosphoric acid*, $H(PO_3)$ remains as a liquid which, on cooling, solidifies to a soft pasty mass ('glacial phosphoric acid'). If the orthophosphoric acid be only heated to about 235°C., less water is driven off and *pyrophosphoric acid*, $H_4(P_2O_7)$, is left as a crystalline mass. Both this pyrophosphoric acid (which is tetrabasic) and the metaphosphoric acid (which is monobasic) yield corresponding series of salts, the pyrophosphates and the metaphosphates. These, however, have reactions different from those of the orthophosphates, and they will be discussed later. Here we are concerned only with the 'phosphates' proper, the salts of orthophosphoric acid.

*Note.*—Compare and contrast this case with that of boric acid above. In both cases the 'ortho' acid, by loss of water on heating, yields 'meta' and 'pyro' acids, but whereas with boric acid we have only one set of reactions (those of metaborates) in the case of phosphoric acid, the different salts give different reactions, as will be seen later.

**Examples of salts (orthophosphates):—**

| | |
|---|---|
| Sodium dihydrogen phosphate (acid salt) | $NaH_2(PO_4)$ |
| Disodium hydrogen phosphate (ordinary salt) | $Na_2H(PO_4)$ |
| Trisodium phosphate | $Na_3(PO_4)$ |
| Calcium phosphate ('Bone Ash') | $Ca_3(PO_4)_2$ |
| Aluminium phosphate | $Al(PO_4)$. |

*Note.*—The tribasic character of phosphoric acid renders possible the existence of three sodium salts. The 'neutral' salt, $Na_3(PO_4)$, has, in solution, an alkaline reaction. The common sodium phosphate is $Na_2H(PO_4)$. One of the most important phosphates is the sodium ammonium hydrogen phosphate $Na(NH_4)H(PO_4)\,4H_2O$, known as 'Microscosmic Salt.' The tendency to form 'mixed' salts is characteristic of phosphoric acid. Another example is the magnesium ammonium phosphate, $Mg(NH_4)(PO_4)$ already noticed (p. 70).

**Solubility of salts.**—The *phosphates* are, as a class, *insoluble in water.* Those of ammonium, potassium and sodium, and also the 'mixed' microcosmic salt, are soluble. There is also a well-known acid phosphate of calcium, corresponding to $NaH_2(PO_4)$, and having the formula $Ca[H_2(PO_4)]_2$ which is soluble in water. It is known as 'superphosphate.'

## Reactions of Phosphates.

[Use powdered dry sodium phosphate for (1) and (2) and a solution of this, or of microcosmic salt, for the rest.]

(1) The dry salt gives *no visible reaction* with **dilute hydrochloric acid.**

(2) The dry salt gives *no visible reaction* with **concentrated sulphuric acid.**

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *yellow precipitate* of silver phosphate, $Ag_3(PO_4)$, which is *readily soluble in cold dilute nitric acid.*

*Note.*—The reaction involves the formation of sodium dihydrogen phosphate, thus :—

$$2Na_2H(PO_4) + 3Ag(NO_3) = Ag_3(PO_4) + 3Na(NO_3) + NaH_2(PO_4).$$

(4) The (neutral) *solution* gives, with **barium chloride** solution, a *white precipitate* of barium hydrogen phosphate, $BaH(PO_4)$, *readily soluble in cold dilute nitric acid.*

(5) If one or two **drops** of a *solution of any phosphate in dilute nitric acid* be added to **2 or 3 ccs.** of **ammonium molybdate** solution, and the mixture be **very gently warmed,** a *crystalline yellow precipitate* (of ammonium phosphomolybdate, see note below) is formed.

*Note.*—The composition of this precipitate is given by

$$(NH_4)_3(PO_4) . 12MoO_3$$

and, as this formula shows, a large excess of the molybdate solution must be present to ensure its formation. That is why the phosphate solution is dropped into the large quantity of the molybdate. Since this test is carried out *in nitric acid solution* it is applicable to phosphates insoluble in water for which Nos. (3) and (4) cannot be used.

## XLI.

## Arsenic Acid and Arsenates.

Formula of acid, $\mathbf{H_3(AsO_4)}$ **Tribasic.**

The compound $H_3(AsO_4)$ is a white crystalline powder, soluble in water. It is, properly speaking, 'ortho-arsenic acid.' When heated it loses water, yielding in turn pyro-arsenic acid, $H_4(As_2O_7)$, meta-arsenic acid, $H(AsO_3)$, and finally (unlike the corresponding phosphoric) the anhydride $As_2O_5$, arsenic pentoxide. Only the ortho-acid and its salts are of any interest or importance.

**Examples of salts** :—

| | |
|---|---|
| Sodium dihydrogen arsenate (acid salt) | $NaH_2(AsO_4)$ |
| Di-sodium hydrogen arsenate (ordinary salt) | $Na_2H(AsO_4)$ |
| Tri-sodium arsenate | $Na_3(AsO_4)$ |
| Lead arsenate | $Pb_3(AsO_4)_2$. |

**Solubility of salts.** — The *arsenates* are, as a class, *insoluble in water.* Those of potassium, sodium and ammonium are however soluble.

## Reactions of Arsenates.

[Use solid sodium (or potassium) arsenate for (1) and (2) and a solution of the same for the rest.]

(1) The dry salt gives *no visible reaction* with **dilute hydrochloric acid.**

(2) The dry salt gives *no visible reaction* with **concentrated sulphuric acid.**

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *terra-cotta coloured precipitate* of silver arsenate, $Ag_3(AsO_4)$, which is *readily soluble in cold dilute nitric acid.*

*Note.*—The reaction here is

$$2Na_2H(AsO_4) + 3Ag(NO_3) = Ag_3(AsO_4) + 3Na(NO_3) + NaH_2(AsO_4)$$

(compare case of phosphate above),

(4) The (neutral) *solution* gives, with **barium chloride** solution, a *white precipitate* of barium arsenate, $BaH(AsO_4)$, readily *soluble in cold dilute nitric acid.*

(5) When one or two **drops** of a *solution of any arsenate in dilute nitric acid* are added to **2 or 3 ccs. of ammonium molybdate** solution there is no immediate precipitate on gently warming the mixture (contrast case of phosphate above), but on **boiling** the solution a *yellow crystalline precipitate* (of ammonium arseno-molybdate) is formed.

*Notes.*—(i) This precipitate has a composition represented by

$$(NH_4)_3(AsO_4) \, . \, 12MoO_3$$

and is in all respects similar to the corresponding one obtained with phosphoric acid (see above).

(ii) An *acidified* solution of any arsenate if treated with *sulphur dioxide* solution (sulphurous acid) and *well boiled,* is reduced to arsenious acid :—

$$H_3(AsO_4) + H_2(SO_3) = H_3(AsO_3) + H_2(SO_4)$$

and this arsenious acid, in the acid solution, gives an arsenic salt (e.g. $As(OH)_3 + 3HCl = AsCl_3 + 3H_2O$) so that on now adding hydrogen sulphide solution the yellow sulphide of arsenic can be precipitated. Phosphates, of course, give no such reaction.

## XLII.

## **Chromic Acid, Chromates** and **Bichromates.**

$$\left.\begin{array}{r}\text{Formula of acid } [H_2(CrO)_4)],\text{ chromic}\\ H_2(Cr_2O_7),\text{ bichromic}\end{array}\right\}\textbf{Dibasic.}$$

The compound $H_2(CrO_4)$ has never been prepared, but there is a large class of salts, the *chromates*, which correspond to it. The crystalline red trioxide of chromium, $CrO_3$, dissolves easily in water, yielding an orange-red, acid solution which behaves as though it contained the acid $H_2(Cr_2O_7)$, but even that compound has not been isolated. The potassium, sodium and ammonium salts corresponding to this acid are, however, well known, and are described as *bichromates*.

**Examples of salts**:—

| | |
|---|---|
| Potassium chromate (yellow) | $K_2(CrO_4)$ |
| Potassium bichromate (red) | $K_2(Cr_2O_7)$ |
| Lead chromate | $Pb(CrO_4)$. |

**Solubility of salts.**—The *chromates*, as a class, are *soluble in water*, but those of silver, mercury, lead, bismuth, zinc and barium are insoluble. The *bichromates* of potassium, sodium and ammonium are *soluble in water*.

## **Reactions of Chromates (and Bichromates).**

[Use powdered potassium chromate or bichromate for (1) and (2), and a solution of potassium chromate for the rest.]

(1) The dry salt give *no characteristic reaction* with **dilute hydrochloric acid** either while cold or when gently heated.

*Note.*—If the mixture be *boiled* (which it should not be) *chlorine* will be evolved due to the oxidation of the hydrochloric acid. Thus, with potassium chromate, there will be (*a*) formation of bichromate, with change of colour from yellow to orange-red:—

$$2K_2(CrO_4) + 2HCl = 2KCl + H_2O + K_2(Cr_2O_7)$$

(*b*) liberation of (bi)chromic acid and oxidation, by this, of the HCl:—

$$\left\{\begin{array}{l}H_2(Cr_2O_7) + 6HCl = 2CrCl_3 + 4H_2O + [3O]\\ [3O] + 6HCl = 3H_2O + 3Cl_2.\end{array}\right.$$

(2) The dry salt gives *no characteristic reaction* with **concentrated sulphuric acid.**

*Note.*—Here again the formation of bichromate from chromate will occur, followed by the liberation of (bi)chromic acid. With much sulphuric acid this may lose water and give the red oxide, $CrO_3$ (chromic anhydride).

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *dark red precipitate* of silver chromate, $Ag_2(CrO_4)$, which is *soluble* (though with slight difficulty) *in cold dilute nitric acid.*

*Note.*—With a solution of a *bichromate* the precipitate formed is reddish-brown silver bichromate $Ag_2(Cr_2O_7)$ but when this is boiled with water, it rapidly changes to the dark-red ordinary chromate :—

$$2Ag_2(Cr_2O_7) + H_2O = H_2(Cr_2O_7) + 2Ag_2(CrO_4).$$

In any case the precipitate of $Ag_2(Cr_2O_7)$ is sufficiently like that of $Ag_2(CrO_4)$ to be recognised as 'silver chromate.'

(4) The (neutral) *solution* gives, with **barium chloride** solution, a *lemon-yellow precipitate* of barium chromate, $Ba(CrO_4)$, readily *soluble in cold dilute nitric acid.*

*Note.*—With a bichromate the precipitate also consists of $Ba(CrO_4)$, and free (bi)chromic acid is formed

$$2K_2(Cr_2O_7) + 2BaCl_2 = [2Ba(Cr_2O_7)] + 4KCl$$
$$[2Ba(Cr_2O_7)] + H_2O = 2Ba(CrO_4) + H_2(Cr_2O_7).$$

(5) If any chromate be **dissolved in dilute hydrochloric acid** the solution acquires the *orange-red* colour of (bi)chromic acid, $H_2(Cr_2O_7)$, and on adding a little **alcohol,** and *boiling* the solution, this orange-red colour disappears, giving place to the *green* colour of chromic chloride, $CrCl_3$.

*Note.*—The alcohol here serves merely as a *reducing agent,* taking the oxygen from the (bi)chromic acid :—

$$H_2(Cr_2O_7) + 6HCl = 2CrCl_3 + 4H_2O + [3O]$$

and being converted into aldehyde :—

$$3C_2H_5(OH) + [3O] = 3H_2O + 3C_2H_4O$$

the sweet fruit-like smell of which is very noticeable.

Any other reducing agent, of course, will serve to effect a similar change of the *orange-red* $H_2(Cr_2O_7)$ into the *green* $CrCl_3$. Instances already noticed are those of *hydrogen sulphide* (see p. 43) and sulphur dioxide (see p. 98).

Other reagents for chromates in solution are soluble lead salts (cf. p. 18) and mercurous nitrate solution (cf. p. 22). Chromates which are insoluble in water cannot be recognized by reactions (3) and (4). It is necessary to boil the powdered salt with **sodium carbonate** solution, filter off the solution (of sodium chromate) produced, acidify it with **acetic acid** (to destroy the excess of sodium carbonate), and then apply tests (3) and (4).

Most chromates are not affected by heat. But mercurous chromate is decomposed thus :—

$$4Hg_2(CrO_4) = 8Hg + 2Cr_2O_3 + 5O_2$$

oxygen being evolved, a sublimate of metallic mercury formed, and a residue of green chromic oxide left. Another special case is that of ammonium bichromate, which decomposes with incandescence thus :—

$$(NH_4)_2(Cr_2O_7) = Cr_2O_3 + 4H_2O + N_2$$

evolving nitrogen and steam, and leaving a residue of chromic oxide.

---

Other acids which belong to Group IV—arsenious and thiosulphuric—will be studied in Chapter IV below.

## ACIDS OF GROUP V.

### XLIII.

### **Sulphuric Acid** and **Sulphates.**

Formula of acid, $\mathbf{H_2(SO_4)}$. **Dibasic.**

The compound $H_2(SO_4)$ is, at ordinary temperatures, a colourless oily liquid of high specific gravity (about 1·83). It is soluble in water in all proportions, and great heat is evolved when the two are mixed.

*Note.—Never add water to sulphuric acid, always vice-versa.*

**Examples of salts** :—

| | |
|---|---|
| Potassium hydrogen sulphate (acid salt) | $KH(SO_4)$ |
| Potassium sulphate | $K_2(SO_4)$ |
| Zinc sulphate | $Zn(SO_4)$ |
| Aluminium sulphate | $Al_2(SO_4)_3$. |

**Solubility of salts.**—The *sulphates* as a class are *soluble in water*. Calcium sulphate is only slightly soluble; mercurous sulphate, and those of barium, strontium and lead are insoluble. There are also basic sulphates of mercury and of bismuth which are insoluble in water.

*Note*.—The majority of sulphates crystallise with 'water of crystallisation,' and their solubility largely depends upon this. Thus copper sulphate, $Cu(SO_4)$, is a white salt, but it combines with water to $Cu(SO_4)5H_2O$, which forms blue crystals and constitutes 'blue vitriol.' Other sulphates form crystals with $7H_2O$—e. g., ferrous sulphate $Fe(SO_4).7H_2O$ ('green vitriol'), zinc sulphate $Zn(SO_4).7H_2O$ ('white vitriol'), and magnesium sulphate $Mg(SO_4).7H_2O$ ('Epsom Salts')—and some with $10H_2O$—e.g., $Na_2(SO_4).10H_2O$ ('Glauber's Salt'). The sulphates of the *trivalent* metallic radicals $Fe^{\cdots}$, $Al^{\cdots}$ and $Cr^{\cdots}$ combine with those of monovalent metallic radicals like $K^{\cdot}$ and $(NH_4)^{\cdot}$, and with water, to form 'double salts' called *alums*, the general formula of which is

$$M_2^{\cdot}(SO_4) . M_2^{\cdots}(SO_4)_3 . 24H_2O.$$

These alums are soluble salts which crystallise alike (in octahedra). The sulphates of *divalent* metallic radicals, like $Fe^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, &c., combine with sulphates of monovalent metals, and water, to form another class of double sulphates known as '*substituted vitriols*,' an example of which is the well-known ferrous ammonium sulphate $(NH_4)_2(SO_4).Fe(SO_4).6H_2O$ ('Mohr's Salt'). These substituted vitriols are also soluble salts which crystallise well and in similar forms (though distinct from that of the alums).

## Reactions of Sulphates.

[Use powdered copper sulphate for (1) and (2) and a solution of this salt for the rest].

(1) The dry salt gives *no characteristic reaction* with **dilute hydrochloric acid.**

(2) The dry salt gives *no characteristic reaction* with **concentrated sulphuric acid.**

*Note*.—Many of the crystallised sulphates when warmed with strong sulphuric acid are deprived of their water of crystallisation and change colour. Thus the blue $Cu(SO_4).5H_2O$ and the green $Ni(SO_4).7H_2O$ become colourless, the red $Co(SO_4)7H_2O$ becomes rose-pink, and so on.

(3) The (neutral) *solution* gives, with **silver nitrate** solution, *no precipitate.*

*Note*.—If the sulphate solution is very strong, silver sulphate, $Ag_2(SO_4)$, which is a sparingly soluble salt, will be precipitated. The reaction with barium chloride—No. 4 below—is, however, so characteristic that this accident should easily be detected, and corrected by repeating No. 3 with a more dilute solution.

(4) The (neutral) *solution* gives, with **barium chloride** solution, a *white precipitate* of barium sulphate, $Ba(SO_4)$, which is *insoluble in cold dilute nitric acid.*

*Note.*—Be very careful to use barium *nitrate* instead of the chloride when the metallic radical has been found to be $Ag^{\cdot}$ or $Hg_2^{\cdot\cdot}$ or $Pb^{\cdot\cdot}$ (see p. 79 above).

(5) The *solution* **acidified with dilute nitric acid** gives, with **strontium nitrate** solution, a *white precipitate* of strontium sulphate, $Sr(SO_4)$, which *appears gradually.*

If the analysis of a salt have shown it to be the sulphate of potassium, or sodium, or ammonium, it is necessary finally to decide whether this salt is an acid sulphate or a neutral one. The reaction of the solution to litmus will give the first indication, and, if the sulphate be an acid one, its solution will effervesce briskly when treated with sodium carbonate. Acid sulphates other than those of $K^{\cdot}$, $Na^{\cdot}$ and $(NH_4)^{\cdot}$ are not commonly met with.

## XLIV.

## Hydrofluoric Acid and Fluorides.

Formula of acid, **HF**. **Monobasic.**

The compound HF, hydrogen fluoride, is a very volatile liquid (it boils at about 19°C.) which is readily soluble in water. The aqueous solution is known as hydrofluoric acid.

**Examples of salts :—**

| | |
|---|---|
| Potassium fluoride | $KF$ |
| Calcium fluoride ('Fluor Spar') | $CaF_2$ |
| Aluminium fluoride | $AlF_3$. |

*Note.*—Though hydrofluoric acid is monobasic and so can only give one salt with a monovalent metal, the alkali fluorides can combine with more HF. Thus we have a salt $KHF_2$ (or $KF.HF$) known as *acid potassium fluoride.* It is by heating this salt that the anhydrous HF is obtained, ordinary potassium fluoride being left behind.

**Solubility of salts.**—Most of the *fluorides* are *insoluble in water*, but those of potassium, sodium, ammonium, silver (aluminium) and mercury are soluble.

*Note.*—The most insoluble fluoride is that of calcium, $CaF_2$. Various 'double fluorides' of which the best known example is sodium aluminium fluoride $Na_3AlF_6$ (or $AlF_3 \cdot 3NaF$) are also very insoluble, the one named constituting the mineral '*cryolite.*'

## Reactions of Fluorides.

[Use powdered calcium fluoride (Fluor Spar) for (1), (2) and (5) and a solution of potassium (or ammonium) fluoride for the rest.]

(1) The dry salt gives *no characteristic reaction* with **dilute hydrochloric acid.**

(2) The dry salt reacts with **concentrated sulphuric acid,** *especially when gently warmed,* in a highly characteristic manner. *Large bubbles* (of hydrogen fluoride vapour) are formed *which move very sluggishly,* and the *liquid will not wet the sides of the tube* but runs off them like water from a greasy surface. The gas *fumes* enormously on coming into the air.

Note.—The alkali fluorides react violently even with cold strong sulphuric acid, but the same peculiar behaviour of bubbles, of liquid and of evolved gas, is observable. It should be noted that the inhalation of hydrogen fluoride vapour is very dangerous.

(3) The (neutral) *solution* gives *no precipitate* with **silver nitrate** solution.

(4) The (neutral) *solution* gives, with **barium chloride** solution, a *white precipitate* of barium fluoride, $BaF_2$, which is *slightly soluble in cold dilute nitric acid* (so that if enough of this reagent be added it may be dissolved).

(5) We have seen that all fluorides when warmed with strong sulphuric acid evolve hydrogen fluoride. Now *hydrogen fluoride attacks glass.* All the varieties of glass are mixtures of silicates and contain, as essential constituent, silica $SiO_2$. It is this which reacts with HF, giving water and the gaseous silicon fluoride, $SiF_4$ :—

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

Thus it is that hydrogen fluoride will **etch** glass. To verify the presence of a fluoride we therefore proceed as follows:—A small quantity of the powdered fluoride is placed in a clean

**lead dish.** A **watch-glass** large enough to cover the dish is **coated,** thinly, **with wax** *on its convex side.* By means of some *finely-pointed* instrument a device of some sort is drawn in the wax, *so as to uncover parts of the glass* in fine lines. Then concentrated sulphuric acid is added to the fluoride in the lead dish, the watch-glass is laid over it, *convex side down,* the concave side is filled with cold water, and dish is *very gently warmed* for a few minutes. On removing the watch-glass, and cleaning off the wax, *the device will be found etched into the glass.*

*Note.*—A *platinum* dish or crucible is, of course, even better than one of lead. Great care must be taken not to overheat and so melt the wax. It is best to support the dish upon a sheet of asbestos with a small circular hole cut in it, so that only the very middle of the dish is warmed.

Another acid of Group V, fluosilicic acid, is dealt with in Chapter IV below.

## ACIDS OF GROUP VI.

### XLV.

### **Nitric Acid** and **Nitrates.**

Formula of acid, **$H(NO_3)$** **Monobasic.**

The compound $H(NO_3)$ is a colourless liquid, having a specific gravity of about 1·5. The 'strong nitric acid' of the laboratory is a solution of this liquid (68%) in water (32%).

**Examples of salts** :—

| | |
|---|---|
| Potassium nitrate ('Nitre') | $K(NO_3)$ |
| Lead nitrate | $Pb(NO_3)_2$ |
| Aluminium nitrate | $Al(NO_3)_3$. |

**Solubility of salts.**—All *nitrates* are *soluble in water.* The only compounds of the acid radical $(NO_3)'$ which are insoluble are certain *basic* nit[illegible] bismuth (see p. 29) and of mercury.

## Reactions of Nitrates.

[Use powdered potassium nitrate for (1) and (2) and a solution of this salt for the rest.]

(1) The dry salt, with **dilute hydrochloric acid**, gives *no characteristic reaction.*

*Note.*—Here again it is essential that the mixture should *not* be *boiled.* If it were, 'aqua regia' would be produced with consequent evolution of chlorine :—

$$\begin{cases} 2H(NO_3) = H_2O + 2NO + [3O] \\ [3O] + 6HCl = 3H_2O + 3Cl_2. \end{cases}$$

(2) The dry salt, with **concentrated sulphuric acid,** gives no reaction while cold, nor even when gently heated, but when *strongly heated* (practically to boiling) there gradually appear *red fumes* of nitrogen peroxide, $NO_2$, arising from the decomposition, at that high temperature, of some of the nitric acid set free.

*Note.*—These red fumes are best seen on removing the tube from the flame and looking down into it. This reaction should be very carefully compared and contrasted with Reaction No. [illegible] of bromides (see p. 84).

(3) The (neutral) *solution* gives *no precipitate* with **silve nitrate** solution.

(4) The (neutral) *solution* gives *no precipit* [illegible] **arium chloride** solution.

*Note.*—Take care to use *barium nitrat* [illegible] of the chloride when the metallic radical has [illegible] $Ag^{\cdot}$ or $Hg^{\cdot\cdot}$ or $Pb^{\cdot\cdot}$ (see page 79).

(5) If an aqueous *solution* of any [illegible] ated with **an equal volume of concentrat** [illegible] ic **acid** and the mixture (which becomes very h [illegible] d and then **ferrous sulphate** solution be pour [illegible] n, so as to form [illegible] er upon the mixture, a *brown* [illegible] seen where the [illegible]

*Note.*—[illegible] reactions which occur are as follows :—(*a*) the nitric acid, set free by the sulphuric, acts as an oxidizing agent upon some of [illegible] ferrous sulphate :—

$$2H(NO_3) = H_2O + 2NO + [3O]$$
$$6Fe(SO_4) + 3H_2(SO_4) + [3O] = 3H_2O + 3Fe_2(SO_4)_3$$

being itself reduced to nitric oxide ; (*b*) this nitric oxide, rising through the liquid, meets with unoxidized ferrous sulphate and combines with it to form the black compound $Fe(SO_4) . NO$.

Conc Sulphuric acid

This reaction must be very carefully compared and contrasted with the corresponding one (No. 5) of *nitrites*, p. 94.

Nitrates give characteristic reactions when they are heated *per se*. The majority decompose into the oxide of the metal, nitrogen peroxide and oxygen, e.g.:—

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

Those of potassium and sodium simply fuse and, at a high temperature, evolve oxygen leaving the nitrite:—

$$2K(NO_3) = 2K(NO_2) + O_2,$$

while that of ammonium is decomposed into steam and nitrous oxide:—

$$(NH_4)(NO_3) = 2H_2O + N_2O.$$

---

Nitrates also deflagrate when heated on charcoal in the blowpipe-flame—see Chapter VI below.

## XLVI.

## Acid and Chlorates.

Formula of acid, $\mathbf{H(ClO_3)}$ **Monobasic.**

The compound $H(ClO_3)$ has never been isolated, and even its solutions in water are very unstable. The corresponding *salts* however, the *chlorates*, are stable and definite.

**Examples of salts:—**

| | |
|---|---|
| Potassium chlorate | $K(ClO_3)$ |
| Barium chlorate | $Ba(ClO_3)_2$. |

**Solubility of salts.**—All the *chlorates* are *soluble in water*.

## Reactions of Chlorates.

[Use powdered potassium chlorate for (1), (2) and (5) and a solution of this salt for the other tests.]

(1) The dry salt does not react with **dilute hydrochloric acid** while cold, but *on warming*, the solution *gradually* acquires the *colour* and *odour* of *chlorine* and its bleaching power.

*Note.*—The chloric acid set free from the chlorate oxidizes the hydrochloric acid :—

$$H(ClO_3) + 5HCl = 3H_2O + 3Cl_2.$$

(2) The dry salt, when treated with **concentrated sulphuric acid,** yields free chloric acid which rapidly decomposes, especially if **very** *gently warmed*, yielding greenish yellow chlorine dioxide :—

$$3H(ClO_3) = H(ClO_4) + H_2O + 2ClO_2.$$

This gas is **violently explosive,** a very slight rise of temperature sufficing to detonate it.

**This experiment must therefore be made with small quantities of material, in a small tube, and must be carried out cautiously.**

(3) The (neutral) *solution* gives *no precipitate* with **silver nitrate** solution.

(4) The (neutral) *solution* gives *no precipitate* with **barium chloride** solution.

(5) A *solution* of any chlorate **acidified with dilute sulphuric acid,** and **boiled with excess of ferrous sulphate,** is *reduced to chloride* which can then be identified by adding **silver nitrate** solution when the curdy white silver chloride will be precipitated.

*Note.*—The reaction is simply that oxygen is taken from the chlorate to oxidize the ferrous into ferric sulphate.

Chlorates also behave in a very characteristic fashion when heated *per se.* They all evolve oxygen (some of them oxygen mixed with chlorine) and leave a residue of the chloride (sometimes mixed with oxide) of the metal.

---

Also, when heated upon charcoal before the blow-pipe they *deflagrate* (see Chapter VI below).

---

Other acids of Group VI—perchloric and permanganic acids—are dealt with in Chapter IV below.

**N.B.—Before attempting to analyse an unknown substance, make a careful study of Chapter V.**

# CHAPTER IV.

## Study of Some Less Commonly Occurring Acids.

## ACIDS OF GROUP I.

### XLVII.

### Ferrocyanic Acid and Ferrocyanides.

Formula of acid, $\mathbf{H_4[Fe(CN)_6]}$. **Tetrabasic.**

The acid itself is a white crystalline solid.

**Examples of salts :—**

| | |
|---|---|
| Potassium ferrocyanide | $K_4[Fe(CN)_6]$ |
| Ferric ferrocyanide (Prussian Blue) | $Fe_4[Fe(CN)_6]_3$. |

**Solubility of salts.**—The *ferrocyanides* as a class are *insoluble in water*, but those of sodium and potassium as well as those of barium, strontium and calcium are soluble.

### Reactions of Ferrocyanides.

[Use dry powdered potassium ferrocyanide for tests (1) and (2) and a solution of the same salt for the other tests].

(1) The dry salt gives *no reaction* with **dilute hydrochloric acid.**

(2) The dry salt, with **concentrated sulphuric acid,** gives no reaction while *cold*, but, *on heating*, *effervesces briskly*, evolving *only* carbon monoxide (burns with a blue flame). No carbon dioxide is evolved (compare oxalates, p. 99).

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *white precipitate* of silver ferrocyanide, $Ag_4[Fe(CN)_6]$ *which is insoluble in cold dilute nitric acid.*

(4) The (neutral) *solution* gives, with **barium chloride** solution, *no precipitate.*

(5) The *solution* gives, with **ferric chloride** solution, a *deep blue precipitate* of ferric ferrocyanide (Prussian Blue), $Fe_4[Fe(CN)_6]_3$.

*Note.*—For reaction of ferrocyanides with ferrous salts see p. 47.

(6) The *solution*, even at great dilutions, gives, with **copper sulphate** solution, a *chocolate-coloured precipitate* of copper ferrocyanide, $Cu_2[Fe(CN)_6]$.

## XLVIII.

### **Ferricyanic Acid** and **Ferricyanides.**

Formula of acid, $\mathbf{H_3[Fe(CN)_6]}$. **Tribasic.**

The acid itself is a brown crystalline solid, soluble in water.

**Examples of salts:—**

| | |
|---|---|
| Potassium ferricyanide | $K_3[Fe(CN)_6]$ |
| Ferrous ferricyanide ('Turnbull's Blue') | $Fe_3[Fe(CN_6]_2$. |

**Solubility of salts.**—Most of the common *ferricyanides* are *soluble in water.* The best known insoluble ferricyanide is that of silver (see below).

### Reactions of Ferricyanides.

[Use dry powdered potassium ferricyanide for tests (1) and (2) and a solution of this salt for the other tests.]

(1) The dry salt gives *no reaction* with **dilute hydrochloric acid.**

(2) The dry salt, with **concentrated sulphuric acid**, gives no reaction while *cold*, but, *on heating*, *effervesces briskly*, evolving *only* carbon monoxide (compare ferrocyanides).

(3) The (neutral) *solution* gives, with **silver nitrate** solution, *an orange precipitate* of silver ferricyanide, $Ag_3[Fe(CN)_6]$, *which is insoluble in cold dilute nitric acid.*

(4) The (neutral) *solution* gives, with **barium chloride** solution, *no precipitate.*

(5) The solution gives, with **ferrous sulphate** solution, a *deep blue precipitate* of ferrous ferricyanide ('Turnbull's Blue'), $Fe_3[Fe(CN)_6]_2$.

For reaction of ferricyanides with ferric salts see p. 48.

## XLIX.

### Sulphocyanic (Thiocyanic) Acid and Sulphocyanides (Thiocyanates).

Formula of acid, **H(CNS).** **Monobasic.**

The acid itself is an unstable liquid of little importance.

**Examples of salts:—**

| | |
|---|---|
| Potassium sulphocyanide | $K(CNS)$ |
| Ferric sulphocyanide | $Fe(CNS)_3$. |

**Solubility of salts.**—The *sulphocyanides* of sodium potassium, ammonium, barium, strontium, calcium and iron (ferric) are *soluble in water*; the other known salts are insoluble.

### Reactions of Sulphocyanides.

[Use dry powdered ammonium sulphocyanide for tests (1) and (2) and a solution of the same salt for the other tests.]

(1) The dry salt gives *no reaction* with **dilute hydrochloric acid.**

(2) The dry salt reacts violently with **concentrated sulphuric acid.** Evil smelling gases, which contain sulphur dioxide, are evolved and sulphur is deposited.

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *white precipitate* of silver sulphocyanide, $Ag(CNS)$, *which is insoluble in cold dilute nitric acid.*

(4) The (neutral) *solution* gives, with **barium chloride** solution, *no precipitate.*

(5) The *solution* gives, with **ferric chloride** solution, *no precipitate*, but *a deep blood-red colouration*, owing to the formation of ferric sulphocyanide, $Fe(CNS)_3$.

> *Note.*—This is a very delicate test. Ferric sulphocyanide is soluble in ether, and if even an extremely dilute solution of a sulphocyanide be treated with ferric chloride, and the mixture be then shaken with ether, the ether layer will be coloured red.

When heated alone, the sulphocyanides of the alkali metals, e.g. $K(CNS)$, melt, and then give a series of colour changes becoming successively yellow, brown, green, and finally blue. On cooling they become white again.

## L.

## Hypochlorous Acid and Hypochlorites.

Formula of acid, **$H(ClO)$**. **Monobasic.**

The acid is only known in dilute aqueous solution. Such a solution is formed when chlorine monoxide, $Cl_2O$, dissolves in water, and can be obtained by shaking chlorine water with yellow mercuric oxide:—

$$2Cl_2 + 2HgO + H_2O = 2H(ClO) + Hg_2OCl_2$$

It is very unstable and is decomposed by light, yielding hydrochloric acid and oxygen.

> *Notes.*—(i) The hypochlorites of the alkali-metals can be obtained by adding to the acid solution the requisite amount of alkali, but they are best made (in solution, and mixed with chloride) by passing chlorine gas into *cold, dilute,* alkali hydroxide solution :—
>
> $$2K(OH) + Cl_2 = K(ClO) + KCl + H_2O.$$
>
> Even in solution, however, the hypochlorites are very unstable salts. If the solution is at all concentrated they react thus :—
>
> $$3K(ClO) = K(ClO_3) + 2KCl,$$
>
> giving chlorate (see p. 117) and chloride. This is what happens

when chlorine is passed into a *hot, strong* solution of an alkali, the hypochlorite first formed immediately reacting further, as above, so that the total effect of the successive reactions is represented by :—

$$6K(OH) + 3Cl_2 = K(ClO_3) + 5KCl + 3H_2O.$$

(ii) The best known commercial hypochlorite is Bleaching Powder or 'Chloride of Lime,' $CaOCl_2$. Its formula shows that it is no simple hypochlorite, but it behaves *in solution* as if it were a mixture of hypochlorite and chloride :—

$$2CaOCl_2 = Ca(ClO)_2 + CaCl_2.$$

It is made by passing chlorine gas over dry slaked lime at the ordinary temperature, and is considered to have the formula $CaCl(ClO)$, thus being a chloride and a hypochlorite in one [This is possible since $Ca^{\cdot\cdot}$ is divalent while each of the acid radicals $Cl'$ and $(ClO)'$ is monovalent].

**Examples of salts**:—

| | |
|---|---|
| Sodium hypochlorite | $Na(ClO)$ |
| Calcium hypochlorite | $Ca(ClO)_2$. |

*Note.*—The name 'calcium hypochlorite' is frequently, though erroneously, applied to bleaching powder.

**Solubility of Salts.**—All *hypochlorites* are *soluble in water.*

## Reactions of Hypochlorites.

[Use dry bleaching powder for (1), and a paste of bleaching powder and water for (2).]

(1) The dry salt *effervesces* with **dilute hydrochloric acid** evolving chlorine gas, recognizable by its colour and by its bleaching action upon wet litmus paper (see p. 83).

It is obviously unnecessary to use strong sulphuric acid as a reagent, since dilute hydrochloric acid gives such a characteristic reaction.

Of reactions in solution it is not possible, in practice, to make effective use of those with silver nitrate and barium chloride, since all the hypochlorites actually employed in the laboratory are mixed with *chlorides* (being obtained from chlorine and alkalis).

(2) A very characteristic reaction of solutions containing hypochlorites is obtained when they are treated with a **drop** (not more) of *cobalt nitrate* solution. The mixture becomes

*black*, and, on warming gently, effervesces, evolving *oxygen*, which will re-kindle a glowing splinter.

*Note.* The tube should be closed with the thumb till the oxygen has accumulated under slight pressure. The reaction which occurs is not known. The black compound is a higher oxide of cobalt, $Co_2O_3$, but how or why it determines the evolution of oxygen from the hypochlorite is doubtful.

## ACIDS OF GROUP II.

### LI.

### Formic Acid and Formates.

Formula of acid, $\mathbf{H(CHO_2)}$. **Monobasic.**

The acid itself is a liquid which freezes at about 8°C., and boils at 100°C. It mixes with water in all proportions. It has a powerful, unpleasant smell, and blisters the skin.

**Examples of salts**:—

| | |
|---|---|
| Sodium formate | $Na(CHO_2)$ |
| Lead formate | $Pb(CHO_2)_2$. |

**Solubility of salts.**—The *formates* as a class are *soluble in water*, the least soluble being those of lead and silver.

### Reactions of Formates.

[Use dry powdered sodium formate for tests (1) and (2), and a solution of this salt for the rest.]

(1) The dry salt gives *no visible reaction* with **dilute hydrochloric acid**, but, on warming gently, the smell of formic acid is perceptible.

(2) The dry salt effervesces with **concentrated sulphuric acid**, evolving *carbon monoxide*, recognized by its burning with a blue flame when lighted.

*Note.*—This production of carbon monoxide is due to the dehydration of the formic acid:—

$$H(CHO_2) - H_2O = CO.$$

(3) The *solution* gives, with **silver nitrate** solution, a *white precipitate* of silver formate, $Ag(CHO_2)$, which rapidly *turns black*, especially on warming.

*Note.*—The black precipitate consists of metallic silver. Its formation is due to the fact that formic acid is a powerful reducing agent:—

$$\begin{cases} 4Ag(CHO_2) + 2H_2O = [2Ag_2O] + [4H(CHO_2)] \\ [2Ag_2O] + [2H(CHO_2)] = 4\mathbf{Ag} + 2H_2O + 2CO_2. \end{cases}$$

(4) The *solution* gives, with **barium chloride** solution, *no precipitate.*

(5) With **ferric chloride** solution, the neutral solution gives a *red colouration* similar to that obtained with acetates (p. 92 above), and a similar precipitate of a basic ferric salt is obtained on boiling the liquid.

## LII.

## Cyanic Acid and Cyanates.

Formula of acid, **H(CNO)**. **Monobasic.**

The free acid is only known as a gas (or vapour) condensable by cooling to a colourless liquid which rapidly changes, even at 0°C., into a hard white solid.

*Note.*—This solid is a polymer of the simple acid H(CNO) and is called cyamelide.

**Examples of salts**:—

| | |
|---|---|
| Potassium cyanate | $K(CNO)$ |
| Lead cyanate | $Pb(CNO)_2$. |

**Solubility of salts.**—The cyanates of the alkali metals and of barium, strontium and calcium are soluble in water. The other known cyanates are insoluble in water.

## Reactions of Cyanates.

[Use powdered potassium cyanate for tests (1) and (2), and a solution of this salt for the other tests.

(1) The dry salt *effervesces* with **dilute hydrochloric acid,** *carbon dioxide* (lime-water test) being evolved, mixed however with a trace of free cyanic acid which gives it a penetrating smell.

*Note.*—The acid sets free cyanic acid, which then reacts with the dilute acid as follows:—

$$H(CNO) + H_2O + HCl = NH_4Cl + CO_2.$$

If, after the reaction, potassium (or sodium) hydroxide solution be added in excess, and the mixture be boiled, ammonia is evolved.

(2) The dry salt, with **concentrated sulphuric acid,** gives a precisely similar reaction.

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *white* curdy precipitate of silver cyanate, $Ag(CNO)$, which is *soluble in cold dilute nitric acid.* [*Contrast silver cyanide*].

(4) The solution gives *no precipitate* with **barium chloride** solution.

## ACIDS OF GROUP III.

## LIII.

## Iodic Acid and Iodates.

Formula of acid, $\mathbf{H(IO_3)}$. **Monobasic.**

The free acid is a white crystalline solid which is formed when iodine is oxidized by boiling it with strong nitric acid:—

$$\begin{cases} 2HNO_3 = H_2O + 2NO + [3O] \\ I_2 + 5[O] = I_2O_5 \\ I_2O_5 + H_2O = 2H(IO_3). \end{cases}$$

**Examples of salts**:—

Potassium iodate $K(IO_3)$.
Barium iodate $Ba(IO_3)_2$.

**Solubility of salts.**—The *iodates* as a class are *insoluble in water.* Only those of the alkali metals are soluble.

## Reactions of Iodates.

[Use powdered potassium iodate for tests (1) and (2) and a solution of this salt for the rest].

(1) The dry salt gives *no reaction* with **dilute hydrochloric acid.**

(2) The dry salt gives *no reaction* with **concentrated sulphuric acid.**

(3) The (neutral) *solution* gives, with **silver nitrate** solution, a *white* precipitate of silver iodate, $Ag(IO_3)$, soluble (with some difficulty) *in dilute nitric acid.*

(4) The (neutral) *solution* gives, with **barium chloride** solution, a *white* precipitate of barium iodate, $Ba(IO_3)_2$, *soluble* (with some difficulty) *in dilute nitric acid.*

(5) If the acidified solution of any iodate be treated with a **reducing agent** (for example, a solution of *sulphur dioxide*) iodine is liberated and is evolved as a violet vapour when the mixture is heated.

*Note.*—Some of the iodic acid is reduced to hydriodic acid :—

$$H(IO_3) + 3SO_2 + 3H_2O = HI + 3H_2(SO_4)$$

and this is then oxidized to free iodine by more of the iodic acid :—

$$5HI + H(IO_3) = 3H_2O + 3I_2.$$

The **action of heat** upon the alkali-metal iodates is simply to expel the oxygen and leave the iodide. But with other iodates, more complex decompositions occur, and *iodine*, as well as oxygen, is evolved.

## LIV.

### **Pyrophosphoric Acid** and **Pyrophosphates.**

Formula of acid, $\mathbf{H_4(P_2O_7)}$. **Tetrabasic.**

### **Metaphosphoric Acid** and **Metaphosphates.**

Formula of acid, $\mathbf{H(PO_3)}$. **Monobasic.**

The production of these two acids, which are both white solids, by heating orthophosphoric acid, $H_3(PO_4)$, has already been described (see Phosphoric Acid, above).

**Examples of salts:**—

Sodium pyrophosphate $Na_4(P_2O_7)$
Sodium metaphosphate $Na(PO_3)$.

**Solubility of salts.**—Both *pyrophosphates* and *metaphosphates* are, for the most part, *insoluble in water.* Those of the alkali metals are, however, soluble, and so is magnesium metaphosphate.

### Reactions of Pyro- and Metaphosphates.

*The reactions of these two classes of phosphates are so similar that they will be considered together.*

[Use the powdered sodium salts for tests (1) and (2) and solutions of them for the rest].

(1) The dry salts give *no reaction* with **dilute hydrochloric acid.**

(2) The dry salts give *no reaction* with **concentrated sulphuric acid.**

(3) The (neutral) *solutions* give, with **silver nitrate** solution, **white** precipitates of silver pyrophosphate, $Ag_4(P_2O_7)$ and metaphosphate, $Ag(PO_3)$, respectively, both of which are *soluble in cold dilute nitric acid.* [Contrast the *yellow* silver orthophosphate].

(4) The (neutral) *solutions* give, with **barium chloride** solution, *white* precipitates of barium pyrophosphate, $Ba_2(P_2O_7)$, and metaphosphate, $Ba(PO_3)_2$, respectively, both of which are *soluble in cold dilute nitric acid.*

(5) The solutions of pyrophosphates and those of metaphosphates both give the **ammonium molybdate** test (see p. 106 above), *but the solution requires to be boiled.*

## Distinction between pyrophosphates and metaphosphates.

A cold solution of a *pyrophosphate*, acidified with *acetic acid does not coagulate* a solution of *albumen.*

A cold solution of a *metaphosphate*, acidified with *acetic acid*, *coagulates* solutions of *albumen* at once.

*Note.*—It is only the *free metaphosphoric acid* which coagulates albumen, hence it is necessary to acidify the solutions.

## ACIDS OF GROUP IV.

## LV.

### Arsenious Acid and Arsenites.

Formula of acid, $\mathbf{H_3(AsO_3)}$. **Tribasic.**

The anhydride of arsenious acid is arsenic trioxide (White Arsenic), $As_4O_6$. It is only very slightly soluble in water, and this solution is regarded as a dilute solution of arsenious acid. The free acid, $H_3(AsO_3)$, has not been isolated. Arsenious oxide dissolves readily in solutions of alkalis, with the formation of arsenites:—

$$As_4O_6 + 12K(OH) = 6H_2O + 4K_3(AsO_3).$$

**Examples of salts:**—

| | |
|---|---|
| Silver arsenite | $Ag_3(AsO_3)$ |
| Calcium arsenite | $Ca_3(AsO_3)_2$. |

**Solubility of salts.**—The *arsenites* as a class are *insoluble in water*, but those of the alkali metals are soluble.

## Reactions of Arsenites.

[Use powdered potassium arsenite for tests (1) and (2) and a solution of this salt in water for the rest.]

(1) The dry salt gives *no reaction* with **dilute hydrochloric acid.**

(2) The dry salt gives *no reaction* with **concentrated sulphuric acid.**

(3) The *solution* gives, with **silver nitrate** solution, a bright *yellow* precipitate of silver arsenite, $Ag_3(AsO_3)$, which is very easily *soluble in cold dilute nitric acid.*

(4) The *solution* gives, with **barium chloride** solution, a *white* precipitate of barium arsenite, $Ba_3(AsO_3)_2$, very readily *soluble in cold dilute nitric acid.*

*Note.*—It will sometimes happen that an aqueous solution of an arsenite which readily gives with silver nitrate solution the yellow $Ag_3(AsO_3)$, does not give any precipitate with barium chloride solution. This is because the arsenite in question is not a 'neutral arsenite' but an acid salt such as $KH_2(AsO_3)$. If an alkali be added cautiously to the mixture of such a solution with barium chloride solution, the barium arsenite will be precipitated *without the solution becoming alkaline* :—

$$2KH_2(AsO_3) + 3BaCl_2 + 4KOH = Ba_3(AsO_3)_2 + 6KCl + 4H_2O.$$

The silver salt could still be formed because silver ortho-arsenite is insoluble in arsenious acid solution :—

$$3KH_2(AsO_3) + 3Ag(NO_3) = Ag_3(AsO_3) + 3KNO_3 + 2H_3(AsO_3).$$

(5) Solutions of arsenites give the reactions numbered (1) and (4), under Arsenic in Chapter II above (*see pp. 35 and 36*).

*Note.*—An arsenite solution, acidified with hydrochloric acid, behaves as a solution of arsenic chloride :—

$$\left\{\begin{array}{l} K_3(AsO_3) + 3HCl = 3KCl + H_3(AsO_3) \\ H_3(AsO_3) + 3HCl = 3H_2O + AsCl_3 \end{array}\right.$$

and, conversely, a solution of arsenic chloride, treated with an alkali, gives a solution of arsenite :—

$$AsCl_3 + 6K(OH) = 3KCl + 3H_2O + K_3(AsO_3).$$

## LVI.

### Thiosulphuric acid and Thiosulphates.

Look up

Formula of acid, $\mathbf{H_2(S_2O_3)}$. **Dibasic.**

The acid itself is unknown. When an acid is added to a thiosulphate, some thiosulphuric acid is probably formed, but it decomposes rapidly according to the following equation:—

$$H_2(S_2O_3) = H_2O + SO_2 + S,$$

sulphur dioxide being evolved and sulphur deposited.

**Examples of salts**:—

| | |
|---|---|
| Sodium thiosulphate | $Na_2(S_2O_3)$ |
| Barium thiosulphate | $Ba(S_2O_3)$. |

**Solubility of salts.**—Most of the known *thiosulphates* are *soluble in water.* The barium salt is only slightly soluble in water while those of silver, mercury and lead are insoluble.

### Reactions of Thiosulphates.

[Use dry powdered sodium thiosulphate for tests (1) and (2), and a solution of the same salt for the rest.]

(1) The dry salt is slowly acted upon by cold **dilute hydrochloric acid,** *sulphur dioxide being evolved and yellow sulphur deposited.* The reaction goes much better if the mixture be warmed.

(2) The same reaction occurs with **concentrated sulphuric acid** (but see Reaction (2), p. 98).

(3) The (neutral) *solution* gives, with *excess of* **silver nitrate** solution, a precipitate which is *white* at first, but rapidly changes in colour, becoming *yellow*, *brown* and *finally black.*

*Note.*—If the silver nitrate be added slowly to the thiosulphate solution, the white precipitate of silver thiosulphate which is formed redissolves in the excess of sodium thiosulphate present in the solution. A permanent precipitate is only obtained by adding an excess of silver nitrate.

The changes of colour are due to the decomposition of the unstable silver thiosulphate, silver sulphide, which is black, being the final product :—

$$Ag_2(S_2O_3) + H_2O = Ag_2S + H_2(SO_4).$$

(4) The (neutral) solution gives, with **barium chloride** solution, a *white crystalline precipitate* of barium thiosulphate, $Ba(S_2O_3)$, which is *soluble in dilute nitric acid*, but is then decomposed with deposition of yellow sulphur.

*Note.*—This precipitate, especially if the solution is somewhat dilute, forms much better if the side of the tube be *rubbed* with a glass rod.

When heated by themselves the thiosulphates of the alkali metals decompose into sulphate, sulphide and free sulphur (see Chapter VI).

## ACID OF GROUP V.

### LVII.

### **Fluosilicic Acid** and **Fluosilicates.**

Formula of acid, $\mathbf{H_2(SiF_6)}$. **Dibasic.**

An aqueous solution of this acid is obtained, along with gelatinous silicic acid, by the action of silicon fluoride upon water :—

$$3SiF_4 + 4H_2O = H_4(SiO_4) + 2H_2(SiF_6).$$

The silicic acid is filtered off, and a strongly acid solution of fluosilicic acid is obtained. If it be attempted to concentrate this solution by boiling it down, the acid decomposes into hydrogen fluoride and silicon fluoride, which volatilize :—

$$H_2(SiF_6) = 2HF + SiF_4.$$

**Examples of salts** :—

| | |
|---|---|
| Potassium fluosilicate, | $K_2(SiF_6)$ |
| Barium fluosilicate | $Ba(SiF_6)$. |

**Solubility of salts.**—Most of the *fluosilicates* are *soluble in water*, the exceptions being the barium and potassium salts which are only very slightly soluble.

## Reactions of Fluosilicates.

[Use powdered sodium fluosilicate for tests (1) and (2), and a solution of this salt for the other tests.]

(1) The dry salt is not appreciably acted upon by **dilute hydrochloric acid.**

(2) The dry salt *effervesces* with **concentrated sulphuric** acid with evolution of silicon fluoride and hydrofluoric acid (compare fluorides, above).

*Note.*—The presence of the silicon fluoride in the evolved gases can be shown by holding in them a small drop of water resting in a loop upon a platinum wire. The $SiF_4$ will react with the water, as shown above, and the drop will become turbid with the gelatinous precipitate of silicic acid.

(3) The (neutral) *solution* gives *no precipitate* with **silver nitrate** solution.

(4) The *solution* gives, with **barium chloride** solution, a *white* crystalline precipitate of barium fluosilicate, $Ba(SiF_6)$, which is *insoluble in cold dilute nitric acid.*

## ACIDS OF GROUP VI.

### LVIII.

### **Perchloric Acid** and **Perchlorates.**

Formula of acid, $\mathbf{H(ClO_4)}$. **Monobasic.**

The acid itself is a volatile colourless liquid which, with the required amount of water, gives a crystalline solid hydrate, $H(ClO_4).H_2O$. This is soluble in water to a very strongly acid solution.

The most important **salt** is

potassium perchlorate $K(ClO_4)$

which is only very slightly soluble in water. The *perchlorates* of all the other common metals are *soluble.*

## Reactions of Perchlorates.

[Use sodium perchlorate for tests (1) and (2), and a solution of this salt for the other tests.]

(1) The dry salt gives *no reaction* with **dilute hydrochloric acid** (contrast chlorates).

(2) The dry salt gives *no effervescence or visible reaction* with **concentrated sulphuric acid** (again contrast chlorates).

(3) and (4). The *solution* gives *no precipitate* with either **silver nitrate** or **barium chloride** solution.

(5) The solution of a perchlorate is *not reduced* to chloride by ferrous sulphate in the presence of dilute sulphuric acid (contrast chlorates).

(6) When strongly heated, perchlorates decompose, *evolving oxygen* and leaving a residue of *chloride.*

*Note.*—Perchlorates (of the alkali metals) are the first products of the action of heat upon the corresponding chlorates :—

$$4K(ClO_3) = 3K(ClO_4) + KCl.$$

At the same time a certain amount of the chlorate decomposes into chloride and oxygen, but the more carefully the heating is done the less does this second reaction occur.

## LIX.

### **Permanganic Acid** and **Permanganates.**

Formula of acid, $\mathbf{H(MnO_4)}$. **Monobasic.**

The compound $H(MnO_4)$ is only known in aqueous solution, which has the characteristic *purple colour of all permanganate solutions.*

**Examples of salts** :—

| | |
|---|---|
| Potassium permanganate | $K(MnO_4)$ |
| Barium permanganate | $Ba(MnO_4)_2$. |

**Solubility of salts.**—All *permanganates* are *soluble in water*, the silver salt being one of the least soluble.

### Reactions of Permanganates.

[Use powdered potassium permanganate for tests (1) and (2), and a dilute solution of this salt for the rest.]

(1) The dry salt, with **dilute hydrochloric acid,** gives no reaction while cold but, *on warming*, *chlorine is evolved.*

*Note.*—If *strong* hydrochloric acid be dropped upon solid potassium permanganate, a steady stream of chlorine gas is evolved. Since this can be regulated by varying the rate at which the hydrochloric acid is supplied, the reaction affords a very convenient method of preparing chlorine. It depends, of course, upon the action of the permanganate as an oxidizing agent (see below).

(2) The dry powdered salt (use *very little*) treated with cold **concentrated sulphuric acid** dissolves, forming a green liquid. If this be *cautiously heated* a slight *explosion*, accompanied by a red flash, occurs, and brown flakes of manganese dioxide are projected from the tube.

*Note.*—The explosive substance is probably the anhydride, $Mn_2O_7$, of permanganic acid. When heated this decomposes suddenly into $MnO_2$ and oxygen.

(3) and (4) The *solution* gives *no precipitate* either with **silver nitrate** or with **barium chloride** solution.

(5) The solutions of permanganates are *powerful oxidizing agents*, especially in the presence of dilute sulphuric acid, when they react thus :—

$$2K(MnO_4) + 3H_2(SO_4) = K_2(SO_4) + 2Mn(SO_4) + 3H_2O + [5O]$$

the oxygen being taken by any reducing agent that may be present, and the purple colour of the permanganate being discharged. Among the many reducing agents which will readily effect this change are ferrous salts, sulphurous acid and sulphites, nitrous acid and nitrites, thiosulphates, sulphuretted hydrogen and soluble sulphides (with separation of sulphur) and, on warming, oxalic acid and oxalates.

*Note on the formation of permanganates.*—When any compound of manganese is fused with an alkali or alkaline carbonate and an oxidizing agent (e.g. with sodium hydroxide or fusion mixture, and sodium peroxide or potassium nitrate) a *green* melt is obtained. This contains the *manganate* of the alkali metal :—

$$2Na(OH) + MnO_2 + [O] = Na_2(MnO_4) + H_2O.$$

The manganates, salts of manganic acid, $H_2(MnO_4)$, are all green and soluble in water. If the cooled melt be extracted with water a green solution is obtained. The manganates are exceedingly unstable, and if their solutions are acidified (e.g. with dilute sulphuric acid) at once yield permanganates, the colour changing from green to purple :—

$$5Na_2(MnO_4) + 4H_2(SO_4) = 4Na(MnO_4) + 3Na_2(SO_4) + Mn(SO_4) + 4H_2O.$$

**N.B.—Before attempting to analyse an unknown substance, make a careful study of Chapter V.**

# CHAPTER V.

## HOW TO CARRY OUT THE ANALYSIS OF A SINGLE SUBSTANCE.

**I.** When confronted with a substance whose composition is unknown it is well first to *note*, and describe in writing, *its appearance* as to colour, state of aggregation and crystalline form (if any). These details may not, in many cases, afford much help in the identification of the substance, but the habit of observing them will tend to impress upon the memory the appearance of many different substances so that, with growing experience, these observations will become increasingly valuable.

**II.** The next step is, usually, to make the experiment of *heating the powdered substance by itself in a hard-glass ignition-tube.* In the next chapter some of the results which may be observed, with the conclusions that may be founded upon them, are summarized. It is strongly recommended that the making of this experiment should be at once recorded in writing, together with a description of the result which follows, whether that result be positive or negative. If it be found possible to draw any conclusions from what has been observed, these also should be placed on record, before any further experiment is attempted.

It cannot be too strongly emphasized that *every experiment which is made in the course of an analysis, together with the results observed and the conclusions (if any) which can be based upon them, ought to be recorded at once in a note-book. If the account of an analysis is not written until after that analysis is completed, the record is apt to contain what the student thinks* *should have been observed rather than what was actually seen, so that any misconception, once formed, is unconsciously perpetuated.*

*If, however, each experiment be considered strictly on its own merits, it is impossible* (granted a reasonable knowledge of reactions) *for a bias toward a false interpretation to persist for very long.*

**III.** With this warning we may proceed to consider what should next be done. Perhaps the simplest and most satisfactory plan is to **examine the solubility of the substance.** Notice that we do not say 'make a solution': that is to follow.

The **solvents** available in ordinary analytical work are :—

(i) **water** (meaning, of course, *distilled* water),
(ii) **dilute hydrochloric acid,**
(iii) **strong hydrochloric acid,**
(iv) **dilute nitric acid**, and
(v) **aqua regia.**

*Note.*—Remember that *aqua regia* is a mixture of strong hydrochloric and strong nitric acids, in the proportion of *four* volumes of the former to *one* volume of the latter. Its action as a solvent is due to its yielding chlorine, produced by the oxidizing action of the nitric acid upon the hydrochloric :—

$$2H(NO_3) = H_2O + 2NO + 3[O]$$
$$2HCl + [O] = H_2O + Cl_2.$$

These solvents should always be tried (as described below) *one after another, in the order here given.* If water will not dissolve a substance, try dilute hydrochloric acid; if that fails, try strong hydrochloric acid; and so on, till this list has been exhausted. Should a substance be encountered that will not dissolve in any of these solvents it can only be analysed by special methods. A few instances of such substances, with examples of methods available for their analysis, are given in Chapter VII below.

**To examine the solubility of a substance.**—Place 10 to 15 ccs. of the solvent to be tried in a clean test-tube, warm it slightly, and add a *small* pinch of the finely-powdered substance. If the substance added does not speedily disappear into solution, heat the mixture. If this small quantity dissolves totally, and remains dissolved on cooling the solution, the substance is soluble in that particular solvent; but if it does not wholly dissolve the substance is to be regarded as insoluble in that solvent.

**IV.** When the substance has been thus proved to be soluble in a particular solvent, the next step is to prepare a solution suitable for analysis. To do this:—About as much of the finely-powdered substance as could be heaped upon a sixpence is taken, and added—*in small portions at a time*—to the 10 ccs. or so of the hot solvent, each portion being allowed to dissolve before the next is added. All the substance thus taken should be dissolved in order to get a solution of convenient strength. Then the solution is cooled to the ordinary temperature, by holding the tube under running water. In most cases the solution is now ready for analysis.

*Notes.*—(i) If the solvent used be strong hydrochloric acid, the cooled solution should be diluted with an equal volume of distilled water before being used for analysis.

(ii) If, in the process of dissolving in acids, a gas be evolved (effervescence) this gas should be at once examined. It may consist of carbon dioxide, sulphur dioxide, nitrous fumes, hydrogen sulphide or chlorine. The characteristics of these gases are described under carbonates, sulphites, nitrites, sulphides (and chlorides) in Chapter III. In all cases except the last-named the gas comes from the decomposition of the salt. Chlorine, if found, comes from the action of some oxidizing agent upon the hydrochloric acid used as solvent.

(iii) In cases where *aqua-regia* is employed as a solvent, chlorine is necessarily evolved (see above) and its evolution gives no information as to the nature of the substance under examination.

(iv) *In all cases where a gas is evolved, the solution must, before it is fit for use, be boiled until it is free from that gas.* Otherwise the gas may react with some of the reagents employed and give rise to confusing results.

(v) There are a few cases in which a gas is evolved and yet the substance does not seem to go into solution. For example, some sulphides contain excess of sulphur and, when they are acted upon by acids, the metallic sulphide is dissolved, with evolution of hydrogen sulphide, while the excess of sulphur remains as an insoluble residue. Similarly thiosulphates, when acted upon by acids, give off sulphur dioxide and leave an insoluble residue of sulphur. In such cases the evolution of the gas proves that solution has taken place, and it is only necessary to boil until the evolved gas is completely expelled, and then to filter, in order to get a clear solution suitable for analysis.

**V.** The solution, once prepared, is then *examined for the metallic radical.* It is advantageous to identify this first because, as soon as its nature is established, useful conclusions can be drawn, from the appearance and solubility of the substance, as to the probable or possible nature of the acid radical.

*Note.*—For this purpose a general knowledge of the solubilities of the most important classes of salts is of the greatest value. Under each acid treated in Chapters III. and IV. above, we have indicated the solubilities of its most important salts, and the student would do well to tabulate these for himself.

The examination for the metallic radical is carried out as follows:—

**(a)** First examine a portion of the solution for the metallic radicals of Group I by means of *dilute hydrochloric acid* (for details see pp. 22 and 23). *If no member of this Group be found,*

**(b)** add to the same portion *hydrogen sulphide solution* to test for the metallic radicals of Group II (for details see pp. 41 and 42). *Should no member of this group be detected,*

*Note.*—It is possible, if the solution taken for analysis was too dilute, to overlook the presence of lead (in Group I.) by failure to obtain the white precipitate of lead chloride. Should this have happened, the $Pb^{\cdot\cdot}$ will be precipitated, *as black PbS,* on the addition of $H_2S$ aq. Since this sulphide of lead is insoluble in yellow ammonium sulphide solution, and since solutions of lead salts give a white precipitate with ammonia solution, the presence of bismuth will naturally be suspected. The *confirmatory tests* will, however, prove that $Bi^{\cdot\cdot\cdot}$ is not present, and then, further confirmatory tests will show that the solution contains $Pb^{\cdot\cdot}$.

**(c)** test a *fresh portion* of the solution, *with ammonium chloride, ammonia and hydrogen sulphide solutions,* for the metallic radicals of Group III (for details see pp. 59 and 60). *Failing any indication in this group,*

**(d)** test another fresh portion of the solution, *with ammonium chloride, ammonia and ammonium carbonate solutions* for the metallic radicals of Group IV (for details see pp. 66 and 67). *If none of these be found,*

**(e)** make separate tests for *magnesium,* then *ammonium,* then *potassium* and finally *sodium,* **in this order** (for details see pp. 69 to 76).

Having determined that a member of a particular Group is present, and having decided which member it is by the methods indicated in the pages quoted, it is essential that at least one, and preferably more that one, *confirmatory test* should be applied so that the evidence may be as complete as possible.

*Notes.*—(i) The warning already given concerning the reactions of acidified solutions of chromates and ferric salts with hydrogen sulphide solution should be carefully borne in mind (see p. 42). Nor should it be forgotten that, if the precaution indicated in *Note* (iv) to Section IV. of this Chapter be omitted, a precipitate of sulphur may sometimes be obtained in testing for the metallic radicals of Group II. (compare *Note* (i) to Section VIII of this Chapter).

(ii) In addition to tests applicable to compounds in solution, various reactions 'in the dry way,' discussed in Chapter VI. below, are of the greatest value as confirmatory tests, and they should be utilized as much as possible.

**VI.** The general principles governing the systematic examination for acid radicals have already been somewhat fully indicated in the introductory portion of Chapter III above. If the account there given has been carefully considered, it should be plain that, for *substances soluble in water*, two methods of identifying the acid radical are immediately available. On the one hand, the reaction of the powdered solid with *dilute hydrochloric acid* (compare p. 77), or, *failing this*, with *concentrated sulphuric acid* (compare p. 78), will in many cases give unmistakeable indications. On the other hand, the reaction in aqueous solution with (a) *silver nitrate*, and (b) *barium chloride* (*or nitrate*) solutions, will serve to group, and frequently to identify at once, the various acid radicals (compare pp. 79 and 80).

Where it is possible to utilize both plans, both should be adopted. But with substances insoluble in water only the former of the two is *directly* applicable. In such cases it should be used, and, if possible, the acid radical should be identified without going to the trouble of preparing a neutral solution suitable for the application of the second method (by boiling with sodium carbonate solution, &c., see paragraph VII below).

In the cases of *salts insoluble in water*, if neither the treatment with dilute hydrochloric acid nor that with concentrated sulphuric acid have given any definite and recognizable indication, it is *probable* that the acid radical is that of a sulphate, $(SO_4)''$, or of a phosphate, $(PO_4)'''$, or of a borate, $(BO_2)'$. These radicals should, under the circumstances, be sought for, one by one, as follows:—

*sulphates*, by testing a *solution* of the substance *in dilute nitric acid* with *barium chloride* (or, in case the metallic radical be $Ag^{\cdot}$ or $Pb^{\cdot\cdot}$ or $Hg_2^{\cdot\cdot}$, *barium nitrate*) solution (see p. 112);

*phosphates*, by adding a *solution* of the substance *in dilute nitric acid* to excess of *ammonium molybdate* solution and warming gently (see p. 106);

*borates*, by making a *solution* of the substance *in dilute hydrochloric acid*, placing a drop of this upon a piece of *turmeric paper* and drying (see p. 104).

**VII.** *Preparation of a neutral solution, for examination with* (a) *silver nitrate*, and (b) *barium chloride solution, from a salt insoluble in water.*

Two or three grammes of the **finely powdered solid salt** are placed in a small flask with 20 ccs. of a **concentrated solution of sodium carbonate** and the mixture is **boiled for five minutes.** By this means a certain amount of the salt is made to enter into double decomposition with the sodium carbonate:—

$$\mathbf{MX} + Na_2(CO_3)\,aq. = \mathbf{M}(CO_3) + Na_2\mathbf{X}\,aq.$$

On filtering, the clear **filtrate** will contain, in addition to the unacted-upon sodium carbonate, some of the (soluble) sodium compound of the acid radical of the salt. A corresponding amount of the metallic radical of the salt will remain, as carbonate, in the **residue** upon the filter paper, together with that portion of the salt taken which has not been acted upon.

The excess of sodium carbonate in the **filtrate** must be destroyed before tests for the acid radical can be applied. This is done by **neutralizing** the liquid (*which is kept hot*) with **dilute nitric acid.** The sodium carbonate reacts as follows:—

$$Na_2(CO_3) + 2H(NO_3) = 2Na(NO_3) + H_2O + CO_2$$

and the carbon dioxide is at once evolved from the hot liquid. We thus obtain, finally, a solution containing only sodium nitrate and the sodium salt of the unknown acid radical. Since nitrates give no precipitate with either silver nitrate or barium chloride solution, any reaction obtained with either of these reagents must be due to the unknown acid radical.

*Note.*—A solution is *neutral* when it neither turns blue litmus red nor red litmus blue. If too much nitric acid should have been added, the neutrality must be restored by cautious addition of *dilute* ammonia solution.

**VIII.** Finally, it must be remembered that, in exceptional cases presented by substances insoluble alike in water and in acids, special methods may be needed for investigating the acidic as well as the metallic radical. Some examples of this kind are given in Chapter VII, below.

*Notes.*—(i) Once again attention is directed to the fact that certain acid radicals are *necessarily* detected in the course of the ordinary tests for metallic radicals.

Thus *carbonates* will be detected when dilute hydrochloric acid is added to their solutions in water, or when the salts themselves are dissolved in dilute acid, by the *effervescence and evolution of carbon dioxide* which then occurs.

*Nitrites,* similarly, should be detected by the *evolution of red-brown fumes* ($N_2O_3$) which occurs when their solutions are acidified, and so should *sulphites,* by the *evolution of sulphur dioxide* which takes place when they are acidified with (or dissolved in) dilute hydrochloric acid. *Hypochlorites* evolve *chlorine* with cold dilute hydrochloric acid.

Even if any of the three last-named had been overlooked at the time of acidifying, it must have been detected immediately afterwards by the copious white precipitate of *sulphur* which followed the addition of hydrogen sulphide solution, and was due to the oxidizing action of the nitrous fumes, sulphur dioxide or chlorine respectively upon the hydrogen sulphide :—

$$H_2S + N_2O_3 = H_2O + 2NO + S.$$
$$2H_2S + SO_2 = 2H_2O + 3S.$$
$$H_2S + Cl_2 = 2HCl + S.$$

*Thiosulphates* should be recognized instantly by the *separation of yellow sulphur (accompanied by evolution of sulphur dioxide)* which always results from the action of dilute hydrochloric acid upon them, especially on warming.

*Chromates* will have been recognized from the fact that their acid solutions have an *orange-red* colour and this, on addition of hydrogen sulphide, *changes to green* with eventual separation of a white precipitate of sulphur, the change being brought about more quickly by warming (compare p. 43).

It should therefore be known, early in the course of an analysis, whether either of the acid radicals $(CO_3)''$, $(NO_2)'$, $(SO_3)''$, $(ClO)'$, $(S_2O_3)''$ or $(CrO_4)''$ [and equally, $(Cr_2O_7)$] is present in a salt. In any such case the examination for the acid radical will merely consist in the extension and *confirmation* of the indications already obtained.

(ii) The reactions given by various classes of salts with dilute hydrochloric acid (most of these being summarized in the preceding note), and with concentrated sulphuric acid, are described in Chapters III. and IV. under each of the acids there mentioned. The student is advised, having verified them carefully, to tabulate them for his own use.

(iii) Some difficulty is occasionally presented by certain *sulphides* which do not dissolve easily in acids. When it is necessary to use aqua-regia as solvent, the dissolution is not accompanied by evolution of hydrogen sulphide, for that compound is at once decomposed (oxidized) with *separation of sulphur*. This sulphur usually collects in the hot liquid, into a globule which, on cooling, forms a yellow bead. Its occurrence indicates the presence of a sulphide.

# CHAPTER VI.

## STUDY OF SOME REACTIONS NOT CARRIED OUT IN SOLUTION.

It will be seen from the preceding chapters that chemical analysis is very largely concerned with reactions occurring between salts, acids and bases *in aqueous solution.* But reference has from time to time been made to other reactions, and other methods of investigation, in which aqueous solutions are not employed. Such reactions are said to be carried out 'in the dry way.'

The first point to be noticed is that, in these reactions, we are usually concerned with the behaviour of substances at high temperatures. For the attainment of these temperatures we depend either upon the *Bunsen burner* or upon the *blow-pipe.*

The **Bunsen burner** consists of a vertical tube provided at its lower end with air-holes, the size of which can be adjusted at will. Coal gas is supplied so as to issue from a fine jet placed also at the lower end of the vertical tube, and so arranged that the rush of gas from the jet draws in air through the air-holes. The size of these latter is regulated so that the mixture of gas and air burns, when ignited, at the top of the tube with a non-luminous flame.

An examination of such a **Bunsen-flame** will show that it consists of two parts. *Inside* is a hollow, excessively thin *cone*, which has a bright *blue* colour. If the air-holes are a little too widely opened, so that the flame roars, this inner cone acquires a greenish-blue colour and is very clearly to be seen. The interior of this cone contains merely the mixture of gas and air which has ascended the tube and is on its way to be burnt. *Outside* this blue cone is a '*mantle*,' the colour of which is *faint purple*, and the thickness of which varies from almost nothing at the base of the blue cone to a maximum at,

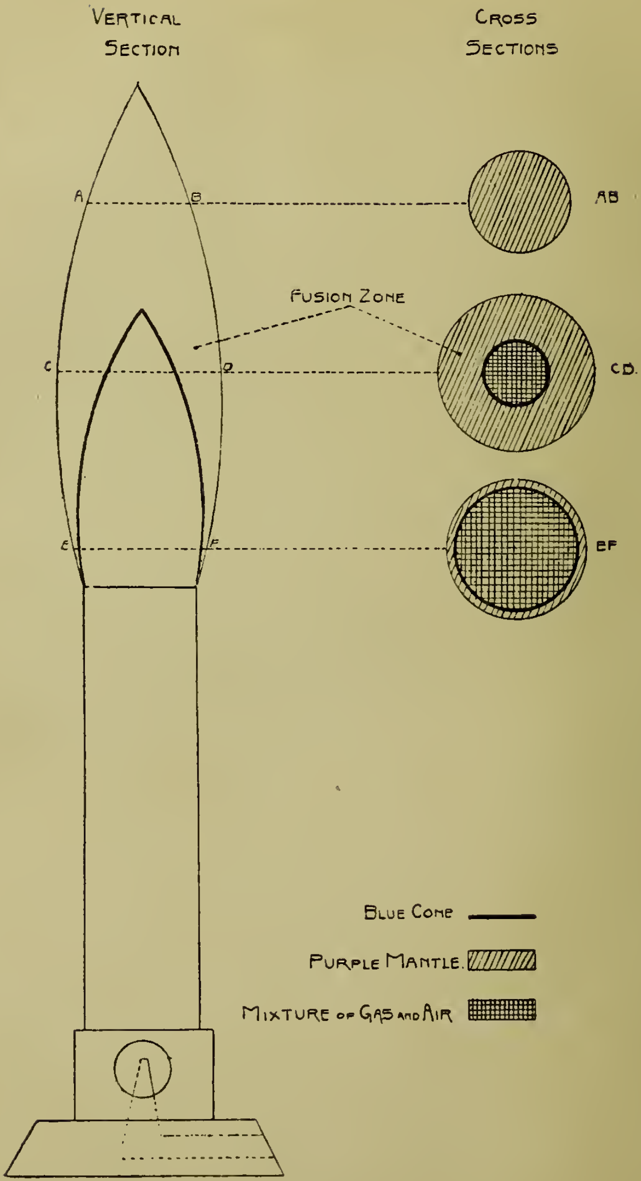
Vertical Section
Cross Sections
A
B
AB
Fusion Zone
C
D
CD.
E
F
EF
Blue Cone
Purple Mantle.
Mixture of Gas and Air

FIG. 1.

or a little above, its top, and then tails off gradually to the topmost point of the flame. It is this outer mantle that is the *hot* part of the flame, and its hottest portion (often described as the 'fusion zone') is almost level with, but just below, the top of the inner blue cone. The diagrams of Fig. 1. give some idea of the structure of the flame.

If the air-holes of a Bunsen burner be gradually closed it is found that, when the air supply is diminished beyond a certain point, there appears, *at the top of the blue cone*, a small *yellow region*, the size of which increases as the air-supply is cut down, until, at last, an ordinary luminous flame is obtained. The yellow portion of a luminous flame contains white-hot particles of carbon, as may be shown by holding a white dish in such a flame when some of this carbon is deposited on the dish as a layer of soot.

Of the various reactions which can be carried out in a Bunsen flame we shall have some examples below.

The **blow-pipe flame** is obtained by directing a fine jet of air into a flat luminous gas flame. The **blow-pipe** is essentially a tube (usually conical) having a mouth-piece at one end and a lateral tube provided with a fine nozzle (preferably of platinum) at the other. To obtain a suitable flat luminous flame, it is usual to drop a brass tube, flattened and slightly grooved at one end, inside the tube of the Bunsen burner so that it covers the jet and no air mixes with the gas before it is burnt. Such a tube is sketched in Fig. 2.

FIG. 2.

The effect of directing a jet of air into such a flame is, if the amount of air blown in be sufficient, simply to transform it into a small but very hot Bunsen flame which, thanks to the arrangement of burner and blow-pipe, can be urged in any desired direction. If the amount of air blown in be not enough to secure the total combustion of the gas, a pointed yellow flame may be obtained.

Now, when the supply of air is more than enough to burn all the gas, an extremely hot non-luminous flame is obtained, which contains, along with the products of combustion, an excess of oxygen. This oxygen is necessarily at a high temperature and will readily combine with any oxidizable substance that is brought in its way. By supplying enough air, then, through the blow-pipe we obtain an **oxidizing flame.**

But if the supply of air blown in is not adequate to secure total combustion, a flame is obtained, having a definite yellow region. The white-hot carbon in this yellow part, if it be made to impinge upon any substance capable of giving up oxygen, will at once take that oxygen and thus act as a *reducing* agent. By supplying, then, a suitable quantity of air through the blow-pipe we obtain a **reducing flame.**

It is very important to be able to obtain either of these two flames at will, and the methods of doing so now described should be carefully noticed and practised.

To obtain an **oxidizing flame, place the nozzle of the blow-pipe well inside the groove at the top of the burner and blow hard.** A finely pointed non-luminous flame results. The blue cone of it is very clearly marked; its mantle is almost invisible. *It is the tip of this mantle* which is the oxidizing flame, par excellence (see Fig. 3).

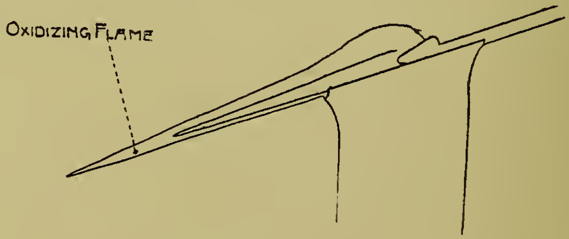

FIG. 3.

To obtain a **reducing flame, hold the nozzle of the blow-pipe just outside the end of the groove at the top of the burner, and blow gently.** A pointed luminous flame is produced, the end of the *yellow* part of which is the reducing flame proper (see Fig. 4).

Reactions which can be effected by the use of one or other of these flames will be described below.

## THE EFFECTS OF HEAT UPON SALTS, ETC.

In many cases the action of heat upon a substance produces changes characteristic enough to furnish very useful information as to the nature or composition of that substance. Since these changes are frequently very striking and simple to observe, it is always well, at the beginning of an analysis, to heat some of the finely powdered substance in a small *hard-glass* ignition tube.

*Notes.*—(i) The substance should be *powdered* because otherwise, if crystalline, it will very likely fly to pieces when heated. This breaking-up, which is usually accompanied by a crackling sound, is called *decrepitation*. It merely shows that the substance is crystalline, and, since this can usually be perceived by mere inspection, is of no great value as a guide to its nature.

(ii) Use *hard glass* for ignition tubes. It is usually difficult, and often impossible, to get a clear indication of the real effect of heating a substance if ordinary glass, which softens easily, is used.

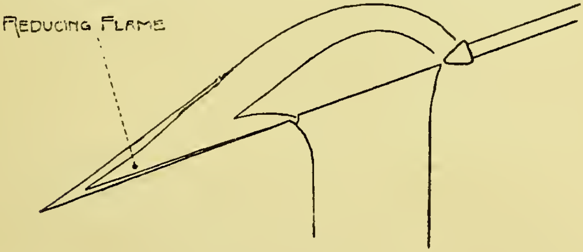

FIG. 4.

There are so many possible effects of heat that even to tabulate them, to say nothing of explaining them, would occupy more space than we can give here. So we shall content ourselves with noticing a few of the most important, most unmistakeable and most instructive. Many others that are not mentioned will, doubtless, be observed from time to time, and they should be noted and thought about, for in this way, with growing experience, the power will be acquired of drawing many other useful inferences from this preliminary experiment.

Some effects of heat are very obvious, but not very important. Salts, for example, which contain *water of crystallization* give it off when heated, and this water *condenses* on the cooler parts of the tube. Frequently, this loss of water is accompanied by a change of colour. Thus, the blue copper sulphate, $Cu(SO_4)\,5H_2O$ becomes white $Cu(SO_4)$ when gently heated, while the pink cobalt chloride, $CoCl_2 . 6H_2O$ is converted into the blue $CoCl_2$.

Another obvious effect *which is very important* is the volatilization of certain substances, the vapour produced usually condensing upon the cooler parts of the tube as a *sublimate.* This **sublimation** is specially characteristic of

compounds of **mercury**
,, ,, **arsenic**
and ,, ,, **ammonium.**

Sublimation may be either total or partial. When total, it implies that the compound as a whole is volatile and the composition of the sublimate is, usually, the same as that of the original substance. When partial, it implies that the compound has undergone some decomposition, and the composition of the sublimate differs from that of the substance heated. An example of this kind is afforded by the thiosulphates of the alkali metals which decompose into sulphate, sulphide and free sulphur:—

$$4Na_2(S_2O_3) = 3Na_2(SO_4) + Na_2S + 4S,$$

the last forming a yellow sublimate. But the really characteristic case is the complete volatilization of many compounds of mercury, of arsenic and of ammonium, followed by more or less complete re-condensation on the cooler parts of the tube.

*Note.*—It must not be supposed that *every* compound of mercury, arsenic and ammonium is totally volatile. Thus mercurous chromate gives a sublimate (a mirror) of metallic mercury and a residue of chromic oxide (see p. 110). Ammonium phosphate leaves a residue containing phosphoric acid, ammonium bichromate leaves chromic oxide (see p. 110), while ammonium nitrate, though totally volatile, gives no sublimate (see p. 116). But the majority of salts containing these basic radicals are volatile.

It is important to examine the sublimate when one is obtained, and this should be done with a lens. For instance, in the case of arsenious oxide the sublimate, where formed on a *warm* part of the tube, is beautifully crystalline, and the appearance of these crystals—which can only be seen with a lens—is exceedingly characteristic.

Of other reactions brought about by heating, the *decomposition of nitrates* (most of which evolve oxygen and red vapours of nitrogen peroxide—see p. 116) and that *of chlorates* (with evolution of oxygen) are easily recognized.

*Note.*—Recall also what has been said above concerning the action of heat upon oxalates (p. 100), tartrates (p. 102), and cyanides (pp. 24 and 89).

## REACTIONS EFFECTED IN THE BUNSEN FLAME.

In order that substances may be heated in a Bunsen flame, a suitable *support* is needed, and, in a very large number of cases, the best is a **platinum wire.** A piece of platinum about 5 cms. (2 ins.) in length is mounted upon the end of a glass rod about 5 cms. long. The wire is fused in, and a small piece of enamel or cement-glass should be used to make a good joint (see Fig. 5). The glass rod is fixed in a small cork so that, when not in use, the wire can be kept in a stout glass sample-tube.

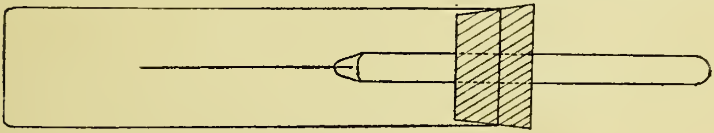

FIG. 5.

*Note.*—The wire should *on no account* be kept dipping in hydrochloric acid (as is sometimes done), for such treatment greatly shortens its ' life.' A platinum wire should always be kept quite *straight.* On the very rare occasions when it is necessary to make a loop in it, this should be done by coiling it round a thin rod, and the greatest care should be taken not to make a sharp bend.

One important use for such a platinum wire is to make *borax beads* upon. Borax is sodium pyroborate (see p. 103) and crystallises, with water, as $Na_2(B_4O_7) . 10H_2O$. When the salt is heated it swells up, gives off its water of crystallization, and then fuses to a clear glass-like mass (anhydrous $Na_2B_4O_7$). Now, when the compounds of various metals are melted with this anhydrous borax, the borates of those metals are formed and, together with the sodium borate, produce a clear 'glass,' which, in many cases, possesses a *distinctive colour.*

When a little borax is made to adhere to a platinum wire (by heating the wire and dipping it, while still hot, into *powdered* borax) and is then heated in the fusion zone of a Bunsen flame, the salt rapidly gives off its water and fuses, forming a drop which remains adhering to the wire and can easily be run along it by slightly inclining the wire and pushing it into the flame (Fig. 6.) or brought back to the end by pointing the wire slightly downwards and drawing it back through the flame (Fig. 7.) This drop when removed from the flame rapidly solidifies to a clear, colourless, glass-like bead—the **borax-bead.**

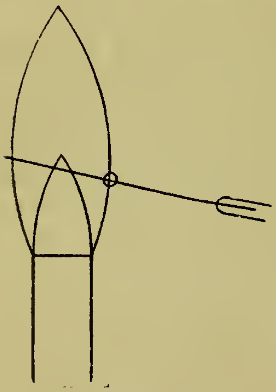

FIG. 6.

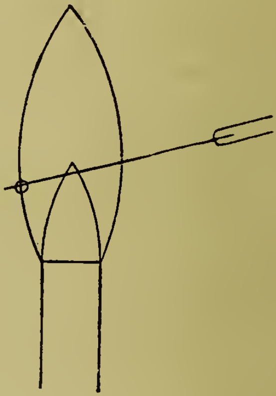

FIG. 7.

If now this bead be dipped into a *fairly strong solution of some salt* (e.g. the sulphate or nitrate) *of copper* and then remelted in the fusion zone of the Bunsen flame, being moved to and fro over half-an-inch or so of the wire (by repeating the movements indicated in Figs. 6 and 7), and finally left again at the tip, it will be seen that the bead has become *coloured.* It is green while still hot, but as it cools it becomes clear *pale blue.* The formation of this pale blue borax bead is *characteristic of the compounds of copper.*

*Note.*—Always make borax beads thus upon a *straight* wire. If a loop be made the bead cannot be moved about, and will be neither so uniform nor so clean. Always notice the colour while hot as well as the final colour attained when cold. Remember that the exact depth of tint will depend upon the quantity of substance introduced, and that it may be necessary to dip the bead twice or more before a definite recognizable colour is shown. It is also possible, but it is not easy, to make these borax-bead tests by dipping the bead into the powdered solid substance; as a rule the result is to pick up too much and obtain a bead which is dark and opaque. In that case the bead must be melted and jerked off the wire and a fresh quantity of borax must be taken. It is a good plan when the making of a bead is completed to melt it and, by a quick downward jerk, shake it from the wire into a clean dry porcelain dish. Its colour is then very clearly to be seen.

There are a number of other metals whose compounds when thus brought into borax beads, and fused there, impart to them characteristic colours. In the following list are given the names of these metals, together with the colours of the borax beads when cold. Care must be taken that the wire is clean, so that the borax bead itself is not coloured before the substance is introduced. This is easily ensured by making a borax bead, running it up and down the wire, and then jerking it off. If necessary this process must be repeated. The colours given by the salts of metals in the following list should be carefully observed, both while the bead is hot, and as it cools. The effect of varying the quantity of substance should also be noticed and recorded.

List of metals whose compounds impart characteristic colours to the borax bead, with the colour of the bead when cold:—

| METAL. | COLOUR. |
|---|---|
| Copper | *Pale blue* |
| Iron | *Yellow* |
| Nickel | *Brown* |
| Cobalt | *Deep blue* |
| Manganese | *Amethyst* |
| Chromium | *Green.* |

*Note.*—It must be remembered that the fusion zone of a Bunsen flame is an 'oxidizing flame,' and that most of the above colours would be different were the bead heated in a 'reducing flame.' This matter will be discussed below (see pp. 156 and 157).

Another use of the Bunsen flame depends upon the volatility of various compounds (particularly the chlorides) of certain metals. There are some of these compounds which, when vapourized, *impart characteristic colours to the flame.* Here again a support, upon which the compound may be brought into the flame, is required, and for this purpose a *clean platinum wire* (see Note (i) below) is most often used, though in some cases an asbestos filament (see Note (ii) below) is to be preferred.

*Notes.*—(i) To clean a platinum wire it is best first to run a borax bead up and down it (as described on p. 152 above) and then to jerk this off as completely as possible while it is molten. This process (repeated if necessary) leaves nothing upon the wire but a little borax. To remove this, the wire is dipped into some *dilute hydrochloric acid* (placed in a clean watch glass) and heated in the fusion zone of the Bunsen flame, the dipping and heating being repeated until the wire glows brightly without imparting any colouration to the flame.

(ii) Asbestos is a fibrous mineral consisting of the silicates of magnesium and calcium [$Mg(SiO_3)$ and $Ca(SiO_3)$]. It is extremely infusible, and is easily pulled apart into thread-like pieces.

To illustrate the method, we may take the case of the **flame colouration** produced by the compounds of *potassium.* Half a gramme or so of any potassium salt, finely powdered, is placed in a watch glass and moistened with a little **dilute** *hydrochloric acid* so as to form a thin paste. Then a *clean platinum wire* is dipped into this paste and *brought into the outer edge of the Bunsen flame, somewhat below the fusion zone.* The flame acquires a very characteristic *lilac colour.*

Another similar case has already been seen during the process of cleaning the wire. The bright *yellow* colour imparted to the flame was due to the fact that borax is a compound of *sodium.*

Any compound of potassium or of sodium will give the flame colouration, lilac or yellow as the case may be. The reason for employing the dilute hydrochloric acid is simply that the chlorides of these metals are very easily volatilized, and so the colour is more intense. But with some other metals it is not only expedient, but actually necessary, thus to employ dilute hydrochloric acid in order to be sure of introducing the *chloride* of the metal into the flame. Thus the metals barium, strontium and calcium will all produce distinct and characteristic flame colourations when introduced *as chlorides* into the Bunsen flame, but many of their compounds are not volatile, and so do not produce any colouration. Hence, to be on the safe side, we always *moisten the compound to be examined with* **dilute** *hydrochloric acid.*

*Note.*—It is not good to use strong hydrochloric acid for this purpose. To see why, take a solution of barium chloride and add to it an equal volume, or rather more, of strong hydrochloric acid. It will then be seen that this chloride, like several others, is insoluble in strong hydrochloric acid.

The following list summarizes the metals whose compounds, when treated as above, give characteristic flame colourations:—

| METAL. | COLOUR OF FLAME. |
|---|---|
| Barium | *Green* |
| Strontium | *Crimson* |
| Calcium | *Orange* |
| Potassium | *Lilac* |
| Sodium | *Yellow.* |

There are other metals whose compounds, when volatilized, impart special colours to the flame. The only one worth notice here is *copper*. The flame-test for copper *should*, however, *not be made upon a platinum wire*—for it will spoil the wire. In this case the asbestos filament is used instead. Moisten any copper compound with hydrochloric acid, dip an asbestos filament into the mixture and bring it into the flame. The flame is coloured a fine **blue,** and the blue portion is edged with *green.*

*Note.*—The blue colour is due to the chloride of copper. The green colour is produced by some other volatile compound formed from the vapour of the chloride and the gases of the flame.

There is another substance which imparts a characteristic colour to the flame, viz. *boric acid*, and this property furnishes another test for borates. The test is carried out as follows :—the powdered borate (e.g. borax) is made into a thick paste with *strong sulphuric acid*, and some of this is taken up on a platinum wire bent into an arc and held **close to,** but NOT IN, the **base** of the Bunsen flame (see Fig. 8 *on next page*). The boric acid (set free from the borate by the strong sulphuric acid) is *volatile* and, as the heat of the flame vapourizes it, passes into the flame and *colours it green.*

*Note.*—The contrast between this green colouration and the yellow one produced when the borax is held *in the flame* is very noteworthy. In the latter case the yellow colour due to the sodium entirely overpowers the green due to the boric acid.

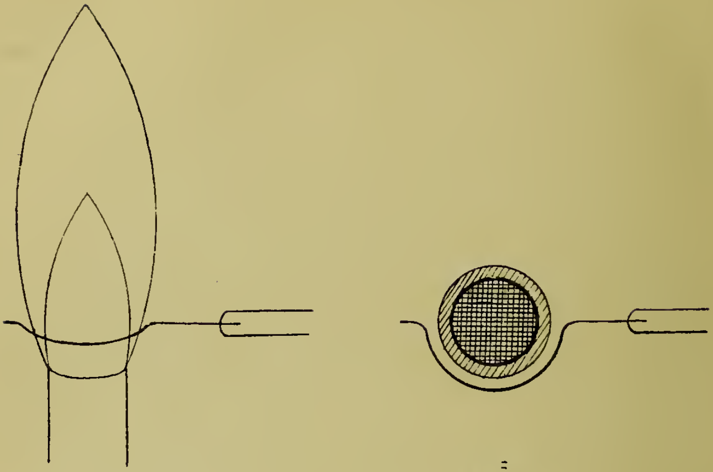

Fig. 8.

## Reactions Effected with the Blow-pipe Flame.

The blow-pipe flame possesses several advantages over that of the Bunsen burner. It is hotter, and it can, at will, be made either powerfully oxidizing or equally strongly reducing in its action.

An illustration of its use, affording good practice in the production of the reducing flame, may be obtained with the borax beads already discussed (see p. 152 above). Prepare a *manganese* borax bead, using enough of a manganese salt to give it a distinct *amethyst* colour. Then heat this bead in the **reducing flame** (see p. 148) of the blow-pipe. It will become *colourless*. On now re-melting it in the **oxidizing flame**, the *amethyst* colour is restored. When these alternations of colour can be obtained easily and certainly, and not till then, the art of producing the reducing and oxidizing flames with the blow-pipe has been mastered.

*Note.*—The maintenance of a steady flame with the blowpipe depends upon learning to breathe through the nose while keeping the cheeks constantly inflated. The knack of doing this can only be acquired by practice.

In a similar way the *brown* bead given by *nickel* compounds becomes *grey* when heated in the reducing flame. The dark blue bead given by compounds of cobalt, and the green one given by those of chromium, are not changed however. Those given by iron and copper compounds, yellow and blue respectively, are harder to reduce. In these cases the reduction is greatly facilitated if the bead is first dipped into a solution of stannous chloride and re-melted in the oxidizing flame. This introduces a trace of tin which acts as an 'oxygen carrier,' and if the bead be now heated in the reducing flame the *yellow* bead containing *iron* becomes *bottle-green*, while the *blue* bead of *copper* becomes *red.*

A little practice with these borax beads will soon give facility in the management of the blow-pipe flame.

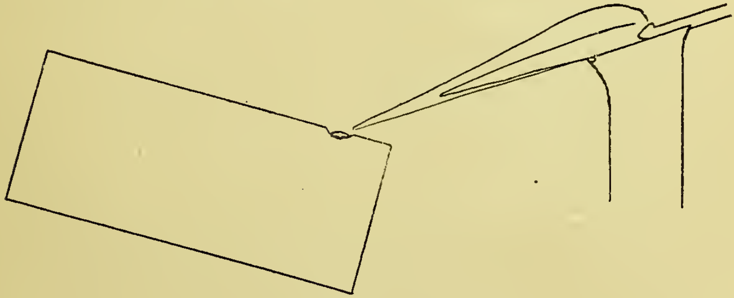

Fig. 9.

The main uses of the blow-pipe flame are, however, to be found in the investigation of the behaviour of solid substances when heated, either alone or mixed with various reagents, upon a suitable support. The support most commonly used is a block of charcoal in which a small shallow hole is bored to contain a little of the *finely-powdered* substance under examination. When it is a question merely of the effect of *heat* upon the substance, it is sufficient to direct upon it the tip of the oxidizing flame (see Fig. 9).

Some substances when thus 'heated on charcoal' give characteristic reactions. Thus, for example, **nitrates** and **chlorates**, as soon as they are at all strongly heated, **deflagrate**, because they give up oxygen which produces a rapid and vivid combustion of part of the carbon support.

In other cases again, the substance heated is decomposed, and yields the oxide of the metal which it contains. To illustrate this, heat a little zinc sulphate strongly in this manner. A residue of *zinc oxide* is left, characterized by the fact that it is *bright yellow while hot*, and becomes *white when cold.* This behaviour furnishes us with another 'test' for salts of zinc.

Few oxides, however, behave in such a very unmistakeable manner as this of zinc, and it is sometimes better, having formed the oxide (as above), to combine it with some other substance so as to produce an easily-recognizable compound. Thus, for example, *aluminium oxide*, which is formed when the sulphate (and many other salts) of that metal are heated on charcoal, is merely a white, infusible solid. But if it be moistened with a little **cobalt nitrate** solution, and again **strongly heated**, it unites with the oxide of cobalt resulting from the ignition of the nitrate, and forms an infusible compound of a fine *blue* colour.

*Note.*—This blue compound, cobalt aluminate, is known as *Thénard's Blue*, after its discoverer.

The *oxide of zinc*, treated in the same fashion, yields a green compound, cobalt zincate, known as *Rinmann's Green.* These reactions are not, as tests, so good as they seem. There are many other substances besides alumina which will give a blue residue when thus ignited after being moistened with cobalt nitrate solution—for example, phosphates like $Ca_3(PO_4)_2$ and silica. The oxide of tin ($SnO_2$) also yields a greenish mass. It is true that these are not really like Thénard's Blue or Rinmann's Green, as the case may be, but they are like enough to be misleading sometimes.

Many salts, when heated on charcoal, do not decompose so as to yield the oxide of their metal. In such cases it is often possible to obtain the oxide by *mixing the salt with dry powdered sodium carbonate*, and heating this mixture before the blow-pipe. A 'double decomposition' occurs, whereby the sodium salt of the acid radical and the carbonate of the metal are formed. The metallic carbonate, at the high temperature, usually loses $CO_2$ and yields the oxide. As an example, let some *ferric phosphate* be mixed intimately with dry sodium carbonate, and a portion of the mixture be gently heated (so as not to fuse it) on charcoal. The reddish colour of the *ferric oxide* formed will be plainly seen on allowing the mass to cool.

If the oxide formed be one which is decomposed by heat it may happen that the metal itself is left behind. Mix a little powdered *silver nitrate* with as much dry sodium carbonate, and heat the mixture strongly on charcoal in the oxidizing flame. A bright bead of *metallic silver* is left, the oxide of silver having been decomposed.

This production of metallic silver suggests that other metallic oxides, even though they may not decompose on mere heating, might be deprived of their oxygen and made to yield their metal by heating them on charcoal with the *reducing-flame* of the blow-pipe. And, in fact, a very considerable number of oxides can easily be reduced to metal in this way. As an illustration, place a small pinch of powdered *lead oxide* in a cavity in a charcoal block and, after making it red-hot in the oxidizing flame, heat it for some time *in the reducing flame*. With very little trouble a *globule of metallic lead* can be obtained which, on cooling, solidifies to a *metallic bead*. This is an instance of an easily reducible oxide, yielding an easily fusible metal. There are other cases in which the metal obtained has so high a melting-point that it does not fuse, but remains as a sort of powder upon the charcoal. Such a case is that of iron. Heat a little powdered *ferric oxide* on charcoal, first in the oxidizing flame until red-hot and then, for some time, *in the reducing flame*. A black powder is left in the cavity which consists partly of *minute specks of metallic iron*. If, after it is cold, this be scraped out of the cavity and put upon a sheet of paper it will be found possible to pick up a great deal of it with a *magnet* and, by looking, with a lens, at the particles adhering to the magnet, to recognize some of them for bits of iron.

In the ordinary course of analysis we have to do, as a rule, not with oxides but with salts, so that, in practice, when we wish to obtain the metal on charcoal, we make an intimate mixture of the substance under examination with dry sodium carbonate, heat this in the oxidizing flame *and then*, having thus formed the oxide, *heat in the reducing flame* to complete the reaction. In this way salts of *lead*, of *copper*, of *bismuth* and of *antimony* will easily yield the respective metals as beads, while those of *iron*, of *nickel*, and of *cobalt*, will furnish metallic powders which are magnetic. In some other cases, particularly that of *tin*, the metal when obtained is so readily oxidized again that considerable difficulty is experienced in getting a bead. This difficulty can be minimized by mixing a powerful reducing agent with the 'melt,' and by far the most effective for the purpose is *potassium cyanide* (see Note (i) below).

*Notes.*—(i) Potassium cyanide, K(CN), acts as a reducing agent because it takes oxygen from many metallic oxides to form potassium cyanate, K(CNO), liberating the metal. Remember that potassium cyanide is very *poisonous.*

(ii) The getting of these metallic beads is largely a matter of practice. For a skilful worker with a blowpipe it is very easy, but it needs a skilful worker in many cases. Very often a number of minute beads are obtained instead of a single large one. It is quite easy to isolate these, as follows:—Cut away the surface of the charcoal, crush it in a folded sheet of paper, and place the powder in a mortar. Then, by running a gentle stream of water over it, wash away the lighter carbon. On draining the heavier residue and placing it upon a piece of blotting-paper the metallic beads, even if very small, are readily seen.

When metallic beads have been obtained, in one or other of the above ways, from a substance given for analysis, they must be examined as to their colour, hardness and malleability in order to identify, as far as possible, the metal of which they are composed. If they are *red*, fairly *hard* and *malleable* they consist of *copper*. *White* metallic beads may consist of silver, lead, bismuth, antimony or tin. If very *brittle*, so that they break up when pressed hard with a pestle upon the bottom of an upturned mortar, they probably consist of *antimony or bismuth*. If *malleable* they may consist of lead or tin or silver. The *lead* beads are not only easily flattened, but are *soft* enough to mark paper. Those of tin and of silver are hard. The *silver* bead is much more easily obtained than that of tin and, when placed on a watch glass with a drop of water and a drop or two of concentrated nitric acid, it dissolves, while that of *tin* is converted into a white insoluble powder (hydrated $SnO_2$, see p. 31).

*Note.*—A similar treatment with nitric acid will serve to distinguish the beads of bismuth and antimony, that of bismuth being soluble while that of antimony is converted into the insoluble oxide (see p. 38).

There are other cases where a metal is readily obtained by reduction on charcoal, but is *volatile* at high temperatures so that, instead of forming a bead, it simply boils away. Such cases are presented by *mercury*, *arsenic*, *cadmium* and *zinc.*

In the cases of arsenic, cadmium and zinc the vapour of the metal burns at once when it comes into the air. The *oxide of arsenic* ($As_4O_6$) is itself very volatile, and appears principally as *white fumes,* which have a powerful and unpleasant *garlic-like smell.* The *oxides of cadmium* (CdO) *and zinc* (ZnO) are not volatile and are, for the most part, deposited as films upon the surface of the charcoal beyond and around the edges of the cavity. *Cadmium oxide* is brown, and so forms a *brown film,* while *zinc oxide,* being white, gives a *white film.*

*Note.*—The zinc oxide is, of course, yellow while hot (see p. 158). It must not be supposed that cadmium and zinc are the only metals whose oxides may thus be deposited as films upon the charcoal. Much the same sort of film (white) can be obtained with antimony, and, to a less extent, lead can give a (yellow) film of lead oxide. The point is that neither with zinc nor with cadmium can metallic beads be obtained.

The following **summary of reactions**, which can be effected **on charcoal with the blow-pipe,** may serve as a brief recapitulation of pp. 156 to 161 :—

(1) *Vivid combustion of part of carbon support in vicinity of heated substance* ('deflagration') *on heating in oxidizing flame,* due to evolution of oxygen from heated substance.

Examples :— **nitrates**
**chlorates.**

(2) *Production of characteristic oxides by heating in the oxidizing flame.*

Example :—

Compounds of **zinc.** Oxide is *yellow* while hot, and *white* when cold.

(3) *Production of characteristic cobalt compounds* by first *heating in oxidizing flame,* then *moistening with cobalt nitrate* solution, and *again heating strongly.*

Examples :—

Compounds of **Aluminium** give *Thénard's Blue*
„ „ **Zinc** „ *Rinmann's Green.*
(p. 158).

(4) *Production of* **metallic bead** *by heating mixture of compound and dry sodium carbonate* **in oxidizing flame.**

Example:—

Compounds of **silver** (p. 159).

(5) *Production of* **metallic bead** *by heating mixture of compound and dry sodium carbonate* first in oxidizing flame till red-hot, and then **in reducing flame.**

Examples:—

| | | | |
|---|---|---|---|
| Compounds of | **lead** | bead | white, malleable, *soft* |
| „ „ | **bismuth** | „ | white, brittle, hard |
| „ „ | **antimony** | „ | white, brittle, hard |
| „ „ | **copper** | „ | red, malleable, hard |

and, with more difficulty (better with potassium cyanide).

Compounds of **tin,** bead white, malleable, hard.
(pp. 159, 160).

(6) *Production, by heating mixture of compound and dry sodium carbonate,* **in reducing flame,** *of volatile metal which gives no beads, but*

either (*a*) *fumes of a volatile oxide,*

Example:—

Compounds of **arsenic** white fume, garlic smell,

or (*b*) *film of oxide upon the charcoal.*

Examples:—

| | | |
|---|---|---|
| Compounds of | **cadmium** | *brown* film |
| „ „ | **zinc** | *white* film (p. 161). |

It must not be supposed that the 'reactions in the dry way' here described—the production of coloured borax beads, the colouration of the Bunsen flame, and the various blowpipe tests on charcoal—by any means exhaust the list of such reactions. On the contrary, they hardly do more than hint at the possibilities opened up by an intelligent use of the Bunsen burner and the blowpipe. But in a book of this size it is impossible to devote enough space to this part of the subject really to do it justice, and the student must refer for more information to larger works.

It may be thought that, seeing how clear and definite many of these 'dry' tests are, how easily carried out and how simply interpreted, it would be better to devote more attention to them, and less to the reactions of metallic and acidic radicals in solution. There is something to be said for this view, but there is more still to be said against it. To take a very simple instance, we have seen that chromium may either form salts as a metal—salts which, in solution, give the reactions of the trivalent metallic radical $Cr^{\cdots}$—or may, in combination with oxygen, give the divalent acidic radical $(CrO_4)''$ whose salts (the chromates) have, in solution, a wholly distinct and different set of reactions. It is not enough merely to find out that a compound contains chromium. We require to know whether that compound is a chromium salt or a chromate. Now the borax bead test will assure us of the presence of chromium equally in chromium sulphate and in potassium chromate. Both will give the green bead. The dry test, alone, does not even hint at any difference between the condition of the chromium in the two salts. And difficulties of this kind, many of them far worse than this, are constantly encountered. Hence, in elementary chemical analysis, it is better to subordinate the information derived from 'dry tests' to that obtainable 'in the wet way.'

This is really the answer, too, that we would give to another question often raised, viz. Is it better to begin by subjecting a salt to dry tests, or to proceed at once to study its reactions in solution? It is *almost always* advantageous for the beginner to start by examining the reactions of the dissolved salt so as to discover its metallic and acidic radicals. Then, various reactions in the dry way will furnish admirable confirmatory tests. It is a great mistake to ignore or neglect these dry tests, for the simple reason that as one progresses in chemical analysis, and has to deal with more and more difficult salts, one is more and more liable to encounter *insoluble* substances—and some of them are fairly common—which will not dissolve either in water or in acids. In dealing with such substances it is not only desirable, but absolutely essential, to have an adequate acquaintance with methods of analysis in the dry way. In the next chapter a few instances of this kind are considered, and a reference to them will show how indispensable reactions in the dry way may become. Therefore we advise that, even in dealing with the easiest and simplest salts, no opportunity should be missed of bringing in Bunsen flame or blowpipe tests as confirmatory evidence. For in this way not only will the analysis be rendered more complete and convincing, but practice in the use of these dry tests will be obtained, leading to a real familiarity with them, and a reasonable facility in carrying them out. The more they are used, the more useful they will ultimately be found.

# CHAPTER VII.

## THE ANALYSIS OF SUBSTANCES INSOLUBLE IN WATER AND ACIDS.

A good many substances liable to be encountered in the study of chemical analysis are quite insoluble alike in water and in acids, resisting even the solvent action of aqua regia. Among them are many minerals, particularly silicates, which are usually of complex composition, containing several metallic radicals, and accordingly not falling within the scope of an elementary work. But there are others which are by no means complex in composition, and a short survey of some of the more common of these will be found useful.

Of the simpler insoluble substances we shall here consider the following:—

| | |
|---|---|
| BARIUM SULPHATE | $Ba(SO_4)$ |
| STRONTIUM SULPHATE | $Sr(SO_4)$ |
| LEAD SULPHATE | $Pb(SO_4)$ |
| CALCIUM FLUORIDE | $CaF_2$ |
| TIN DIOXIDE | $SnO_2$ |
| ANTIMONY OXIDE | $Sb_2O_4$ |
| ALUMINA | $Al_2O_3$ |
| SILICA | $SiO_2$ |
| CHROMIC OXIDE | $Cr_2O_3$ |
| PRUSSIAN BLUE | $Fe_4[Fe(CN)_6]_3$ |
| CARBON | |
| SULPHUR | |

This list, which is intended to be representative, not exhaustive, includes several substances which *may* be soluble in acids under certain conditions. Thus, for example, lead sulphate when made by precipitation is slightly soluble in dilute nitric acid, and calcium fluoride prepared by precipitation is soluble enough in hydrochloric acid or aqua regia to give the reactions of calcium (anomalous precipitation in Group III, etc., see p. 60). The oxides of tin, antimony, aluminium, chromium and silicon *can* exist in acid-soluble forms. But in all these cases if the compound has at any time been subjected to a high temperature it becomes quite insoluble and the naturally occurring forms of lead sulphate ('*Anglesite*'), Calcium fluoride ('*Fluor Spar*'), Tin dioxide ('*Cassiterite*'), Alumina ('*Corundum*,' &c.), and Silica ('*Quartz*,' &c.) are always in this insoluble condition. Similarly the oxide of antimony ($Sb_2O_4$) and the green oxide of chromium, after having once been heated, are totally insoluble.

An insoluble substance encountered in elementary work is very likely to be one of the above, but it evidently does not follow that a substance more or less soluble in acids cannot be one of those named.

The first point to be noticed is that the **colour** of an insoluble substance will give some information about it. Of the twelve substances named only four are really *coloured*. It is impossible to mistake the *green* of chromium oxide, the *dark blue* of Prussian Blue, the *black* of carbon, or the *yellow* of sulphur.

*Note.*—The so-called 'milk of sulphur' is white or nearly so, but after being melted and allowed to solidify it acquires the ordinary yellow colour of the element.

The other compounds are all *white*, for, although some of them, as they occur naturally in the massive form, are apt to be tinted by traces of foreign substances, they all give *white powders* when ground up.

*Note.*—Natural strontium sulphate is known as 'celestine' from the blue colour of its crystals. 'Fluor spar' is commonly found coloured purple or else green. Alumina may be coloured as it is in the precious stones 'ruby,' 'sapphire' and 'amethyst,' and even crystalline silica may be tinted as in 'rose quartz,' 'smoky quartz,' and so on. In all cases these colours are due to the presence of the merest traces of various substances—usually metallic oxides—so small as not to affect the ordinary chemical behaviour of the mineral.

Assuming, for the moment, that the substance is **not coloured,** and excluding therefore the four mentioned above, we can begin to differentiate the others by *heating a little of the powdered substance in a small hard-glass ignition-tube.* Of the eight substances only two, the oxides of tin and of antimony, are appreciably affected.

*Tin dioxide does not melt but becomes yellow while hot* and white again on cooling. *Antimony oxide melts, to a deep yellow liquid,* which solidifies again to a white solid on cooling.

If either of these phenomena be observed the substance should be tested further for tin or for antimony, as the case may be. For example, metallic beads may be obtained on charcoal (see pp. 159, 160) and, from their properties, identified as the one or the other of these metals. A tin bead can be dissolved in (a *little*) strong hydrochloric acid and the solution will give the tests for stannous salts. An antimony bead will dissolve in a mixture of dilute nitric and tartaric acids (see p. 38) and the solution will give the characteristic orange sulphide.

But if there is no apparent effect of heat upon the substance it may be inferred not to consist of tin or antimony oxide, and it is necessary to find further reactions to distinguish between the sulphates of barium, or strontium, or lead, the fluoride of calcium, and the oxides of aluminium or silicon.

Of these, *lead sulphate,* when *mixed with sodium carbonate and heated on charcoal in the reducing flame* of the blow-pipe, will yield metallic beads, easily recognised as consisting of lead. Neither of the other five will thus yield metallic beads. One of the beads may be dissolved in (a *little*) nitric acid, and the solution (after boiling off the excess of nitric acid and diluting with a little water) will give the reactions of lead salts.

One of the remaining five, *calcium fluoride,* when *warmed with strong sulphuric acid,* will give the very characteristic reaction of a fluoride (see p. 113) and is thus easily distinguished.

The four substances still remaining comprise two *sulphates,* $Ba(SO_4)$ and $Sr(SO_4)$, and two *oxides,* $Al_2O_3$ and $SiO_2$. The distinction between them may be effected in many ways. Both the sulphates are those of metals whose chlorides colour the Bunsen flame, but their insolubility renders the direct application of the test doubtful or useless. It is easy to find out whether we have to do with one of the two sulphates, as follows:—a little of the powdered substance is mixed intimately with dry sodium carbonate and powdered charcoal, the mixture is put into the bulb of a small *hard-glass* ignition tube and heated to bright redness (with the blow-pipe flame). If the substance be the *sulphate* of barium or strontium, *the charcoal will*, at the high temperature, *reduce it to sulphide*, some of which will react with the molten carbonate of sodium, e.g.

$$\left\{\begin{array}{l} Ba(SO_4) + 4C = BaS + 4CO \\ BaS + Na_2(CO_3) = Ba(CO_3) + Na_2S \end{array}\right.$$

On allowing the tube to cool, breaking the bulb, and extracting the contents with *a little* water, a solution is obtained (it may be filtered, using a very small filter-paper) which gives the reactions of a soluble *sulphide*—e.g., produces a *black stain* (of $Ag_2S$) when placed *on a silver coin*

$$2Ag + Na_2S + H_2O + O(\text{from air}) = Ag_2S + 2Na(OH)$$

and gives a black precipitate (of PbS) when added to an alkaline solution of lead hydroxide (see p. 90 above). This production of sulphide will show that *either* barium sulphate *or* strontium sulphate is present.

The failure to obtain any of these reactions would indicate, finally, that the white powder in hand was either alumina or silica. With regard to these two we shall have more to say below, but, for the moment, we have to consider how our analysis is to be made complete and convincing when we have by dry tests, as above, been led to infer that a particular substance is $Pb(SO_4)$ or [$Ba(SO_4)$ *or* $Sr(SO_4)$] or $CaF_2$. For the evidence we have acquired, though conclusive enough as far as it goes, is not really satisfactory, as to quantity, in any one case. Thus we may *know* that the only totally insoluble simple fluoride is that of calcium, may *prove* a given substance to be totally insoluble and also to be a fluoride, and so *infer* quite justly that it must be calcium fluoride. But we have not really made an analysis of it. And it is much the same with the others.

Now, the insolubity of these salts is not due either to their basic or to their acidic radicals singly. Many barium salts, for example, are soluble in water and so are most sulphates.

It is the concurrence of a particular metallic and acidic radical in one salt that makes trouble. To get them into solution we must separate these radicals, combining the metallic radical with a different acid, and the acid radical with a different metal. In all the four cases named (and in other similar ones) this is done *by fusing the salt with dry sodium carbonate.*

> *Note.*—In practice we use *a mixture of sodium carbonate and potassium carbonate* (known as '*fusion mixture*') because such a mixture melts more easily than either carbonate alone. The chemistry of the process is, of course, just the same as if one alone were used.

In this way a partial redistribution is effected, a great deal of the salt reacting with the alkali carbonate to give the carbonate of the heavy metal and the sulphate (or fluoride, as the case may be) of the alkali metal—e.g.

$$Ba(SO_4) + Na_2(CO_3) = Ba(CO_3) + Na_2(SO_4).$$

The carbonates of the heavy metals are insoluble in water. The sodium salts are all soluble in water. Thus the action of *water* upon the cooled 'melt' *will separate the metallic radical* (as insoluble carbonate) *from the acidic radical* (as soluble sodium salt). It is only necessary to extract the melt with a reasonable volume of water, and, when it is well disintegrated, to *filter*. Both the residue upon the paper and the filtrate must of course be preserved. The **filtrate** contains (in addition to the excess of alkali carbonate) the sulphate (or fluoride) of sodium. It is *acidified with acetic acid* (to destroy the excess of carbonate) and tested with **barium chloride** solution for sulphate (p. 112) or fluoride (p. 113). The **residue** contains the carbonate (of $Pb^{\cdot\cdot}$ or $Ba^{\cdot\cdot}$ or $Sr^{\cdot\cdot}$ or $Ca^{\cdot\cdot}$). It must be **well washed** with warm water, until the runnings are no longer alkaline to turmeric paper, showing that the adhering alkaline solution has been removed.

> *Note.*—If this washing be neglected, as soon as the carbonate comes to be dissolved in an acid the soluble sulphate (or fluoride) will react with the salt formed and reproduce the original salt.

Then the carbonate is dissolved in as little warm dilute acetic acid as possible and the solution obtained is tested for $Pb^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$ or $Ca^{\cdot\cdot}$, as the previous reactions may have indicated, in the usual manner.

> *Note.*—If the presence of $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$ or $Ca^{\cdot\cdot}$ be suspected, reserve a little of this solution for the *flame-test* (which it will easily give if treated with hydrochloric acid).

It only remains, so far as the white insoluble substances mentioned above are concerned, to distinguish between *alumina* and *silica*. A simple distinction between these is to be found in their behaviour when heated in **a bead of microcosmic salt** on a platinum wire.

> *Note.*—Microcosmic salt is *sodium ammonium hydrogen phosphate*, $Na(NH_4)H(PO_4) . 4H_2O$. When it is heated it loses water and ammonia, leaving sodium metaphosphate :—
>
> $$Na(NH_4)(PO_4) . 4H_2O = Na(PO_3) + NH_3 + 5H_2O.$$
>
> This metaphosphate fuses to a very mobile liquid and *the bead must be made in a looped wire* (see Note on p. 151 above). It behaves on the whole very like a borax bead.

In such a bead *alumina* is, at a red heat, entirely *soluble*, giving a clear glass-like bead, but *silica does not dissolve*. It remains floating in the clear bead and, if present in sufficient quantity, renders it turbid. It is best to introduce only a moderate quantity, heat strongly (with the oxidizing flame of the blowpipe), and to look with a lens for the specks of undissolved silica in the solidified bead.

To distinguish more clearly between these two oxides advantage may be taken of the fact that fused potassium hydrogen sulphate, $KH(SO_4)$, will, at a moderately high temperature, attack alumina, converting it into the sulphate which is soluble in water, while silica is not transformed by this reagent into a soluble compound.

The test should be carried out as follows:—Five or six grammes of acid potassium sulphate are melted in a porcelain crucible and a small quantity (from a half to one gramme at most) of the powdered solid is added, the whole being fairly strongly heated over a Bunsen flame for five minutes or more. Then the mass is allowed to cool, and the crucible is placed in a beaker and boiled with water. If the powder added was *alumina* the whole *product will dissolve completely in the water*, and the clear solution will give the reactions characteristic of aluminium salts (pp. 56 and 57 above). But if it was silica it will still remain insoluble in water, and be left as a pulverulent residue.

> *Note.*—The acid sulphate of potassium, when heated, decomposes (at about 300°) into water and the pyrosulphate :—
>
> $$2KH(SO_4) = H_2O + K_2(S_2O_7)$$

and the latter, at a higher temperature, gives potassium sulphate and sulphur trioxide :—

$$K_2(S_2O_7) = K_2(SO_4) + SO_3.$$

The last-named, at the high temperature, can combine with the alumina to form aluminium sulphate :—

$$Al_2O_3 + 3SO_3 = Al_2(SO_4)_3.$$

Silica, being an *acidic* oxide (an anhydride) does not combine with the acidic oxide $SO_3$ to form a salt.

*Silica* can finally be identified by mixing it, in a clean *leaden dish*, with *powdered fluor spar* and *concentrated sulphuric acid* and warming gently. Silicon fluoride is formed, as gas which fumes strongly in the air, and if a *drop of water*, held in a loop of platinum wire, be placed in the escaping gas, the drop is rendered thick and turbid from the formation of gelatinous silicic acid :—

$$3SiF_4 + 4H_2O = H_4(SiO_4) + 2H_2(SiF_6)$$

(compare pp. 113 and 133 above).

If the insoluble substance encountered be one of those mentioned above as **coloured,** a mere inspection of the colour will give at once a plain indication of its probable nature.

**Sulphur** is *yellow*. It is characterized by its remarkable behaviour when gradually *heated in a dry test-tube*. It first melts to a clear, amber coloured, mobile liquid. As this is further heated it darkens and becomes viscous. After a while (at about 260°C.) it is so thick that the tube may be inverted without pouring any out. On heating still further the sulphur again becomes a mobile liquid, but remains very dark in colour. Finally (at about 440°C.) it boils, giving a reddish vapour which condenses on the cooler part of the tube to form a yellow sublimate. Moreover, sulphur is readily *combustible*, burning in the air with a pale blue flame to form *sulphur dioxide*, a gas of very characteristic smell. The element, in its ordinary forms, is also *soluble in carbon disulphide*, and if a little of the solution be left upon a watch glass (in a fume cupboard) the solvent evaporates and *octahedral crystals* of sulphur are left.

*Note.*—These properties of the element furnish ample means of identifying sulphur, but it may also be recognized by *boiling with slaked lime and water*. It goes into solution as calcium sulphide, and this solution dissolves more sulphur, forming polysulphides of calcium. On filtering, a clear yellow solution (of these latter) is obtained. This solution exhibits the reactions of soluble sulphides see p. 90) and also gives a white precipitate of 'milk of sulphur,' when acidified.

**Carbon** is recognized not only by its total insolubility and *black* colour, but also by its combustibility and by its reducing power. To illustrate the combustibility, a *little potassium nitrate* should be heated in a small iron spoon and the supposed carbon added in **very small portions at a time.** There is a vivid *deflagration* at each addition, and the residue will finally consist to a large extent of potassium carbonate,

$$4K(NO_3) + 5C = 2K_2(CO_3) + 2N_2 + 3CO_2,$$

which may be recognized by its effervescence with acids. To illustrate the reducing power of carbon it may be mixed with powdered cupric oxide and the mixture heated in a hard-glass ignition tube. The black copper oxide will be seen to change to red metallic copper while a gas is evolved which, if it be led into lime water, turns that reagent milky:—

$$2CuO + C = 2Cu + CO_2.$$

**Prussian Blue** is easily known by its *dark blue* colour and the reddish, copper-like lustre which is exhibited by coherent lumps of it. With *strong sulphuric acid* it gives the characteristic reaction of a *cyanide* (see pp. 88 and 119) and it imparts the colours characteristic of iron salts to the borax bead (see pp. 153 and 157). To analyse it, the basic radical $Fe^{\cdot\cdot\cdot}$ must be separated from the acid radical $[Fe(CN)_6]''''$, and this is best effected by *boiling it with potassium* (or sodium) *hydroxide* solution. Double decomposition ensues:—

$$Fe_4[Fe(CN)_6]_3 + 12K(OH) = 4Fe(OH)_3 + 3K_4[Fe(CN)_6],$$

reddish-brown ferric hydroxide being produced, while potassium ferrocyanide is formed in solution. On *filtering*, the **filtrate,** after being *acidified* with dilute hydrochloric acid, will give the characteristic chocolate-coloured *cupric ferrocyanide* when tested with a solution of copper sulphate (see *Note* below), while the **residue,** after having been **thoroughly washed** (with hot water, till the runnings are no longer alkaline) can be dissolved in dilute hydrochloric acid, yielding a solution which will give the reactions of ferric salts (e.g. the blood-red colour with sulphocyanide—see p. 48, and also the *Note* below).

> *Note.*—It is not legitimate to test the acidified filtrate for ferrocyanide with ferric chloride, nor must potassium ferrocyanide be used as a test for ferric iron in the solution of the residue. In analysing Prussian Blue it is obviously improper to use tests that produce this very compound.

**Chromic oxide** is known by its *green colour.* Some salts of chromium resemble it, but they are soluble in acids. It gives to the *borax bead* the characteristic green colour (in both oxidizing and reducing flames—see pp. 153 and 157). To identify it finally, it must be brought into solution, and this can be done best by *oxidizing it in the presence of an alkali*, when an *alkali chromate* is formed. Some solid *sodium* (or potassium) *hydroxide* is *melted* in a clean iron spoon, the supposed chromic oxide is added and then an oxidizing agent, best *sodium peroxide* or, failing this, powdered potassium nitrate, is added *in* **small** *portions* at a time, till a clean dark yellow 'melt' is obtained. This consists of sodium (or potassium) chromate (with any excess of the alkali hydroxide):—

$$4Na(OH) + Cr_2O_3 + [3O] = 2Na_2(CrO_4) + 2H_2O.$$

After cooling, the melt is dissolved in water, and the yellow solution—filtered, if not quite clear—is just *acidified* with acetic acid (to get rid of any free alkali). It will then give the reactions of chromates (see p. 109).

> *Note.*—If the alkali chromate solution be first reduced it becomes possible to apply the tests for the metallic radical $Cr^{\cdots}$. To effect the reduction it is acidified with dilute hydrochloric acid and then boiled, with the occasional addition of a drop of alcohol till it is clear green (cf. p. 109).

Hill

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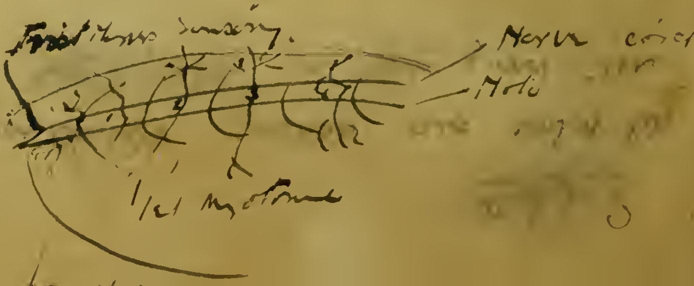
The Present course. Has little motor all along its course

Segmental Nerves. Important. Nerves come off all the way along nerve. Consist of dorsal and ventral root. Amphioxus the not Bilaterally symmetrical. not really internally. In Amphioxus muscle segments are opposite not in alternate. due to locomotion. Very agile animal. This alternation has affected nervous system. Dorsal and ventral root are separate. Muscle fibres and muscle plate. Nerves. Eff. and Aff. No distinct ganglion in Dorsal root. Function of mixed dorsal. Aff and carrying Eff impulses to the muscles and are canals.

General Dis [illegible] nerves.

First two nerves come out from the brain in front of the myotome.



Nervation of the oral hood. Bilat. Symmet

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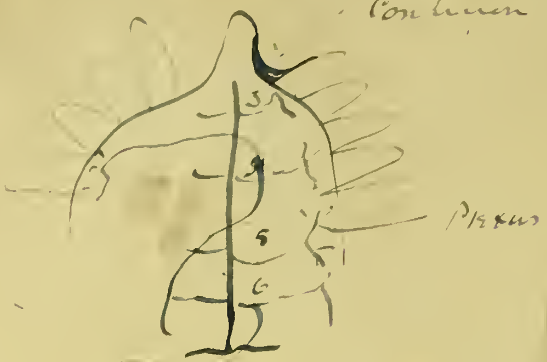

Nol cord supplies , nerves from the
rt side only

Plexus on left side. Plexus on right side
supplied by left side